

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number
WO 01/44796 A1

(51) International Patent Classification⁷: **G01N 27/12** (74) Agent: ALBOSZTA, Marek; 45 Cabot Ave., Suite 110, Santa Clara, CA 95051-6670 (US).

(21) International Application Number: **PCT/US00/42186**

(81) Designated State (national): JP.

(22) International Filing Date:
15 November 2000 (15.11.2000)

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(25) Filing Language: English

Published:

(26) Publication Language: English

- *With international search report.*
- *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

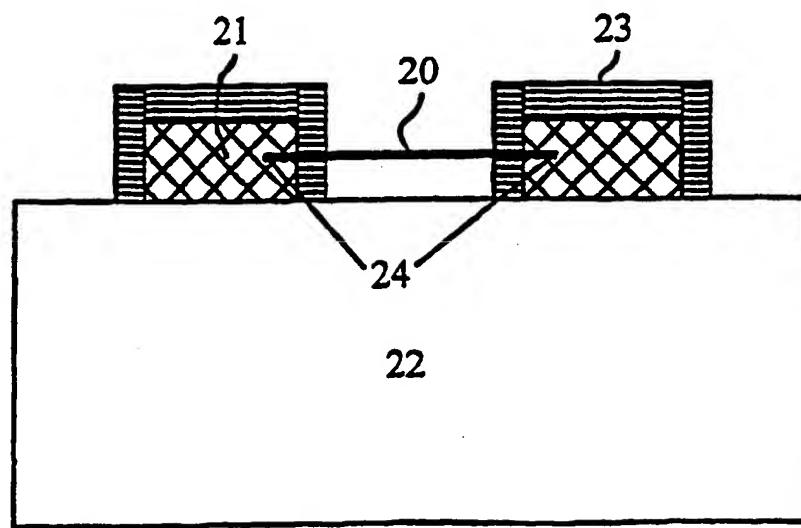
(30) Priority Data:
60/171,200 15 December 1999 (15.12.1999) US

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(71) Applicant: **BOARD OF TRUSTEES OF THE LEAND STANFORD JUNIOR UNIVERSITY [US/US]; 900 Welch Road, Suite 350, Palo Alto, CA 94304 (US).**

(72) Inventors: **DAI, Hongjie; 365 Pescadero Tr., Sunnyvale, CA 94086 (US). KONG, Jing; 879 Roble Ave., Apt. 5, Menlo Park, CA 94062 (US).**

(54) Title: CARBON NANOTUBE DEVICES



(57) Abstract: This invention provides an assembly of novel nanotube devices that can be employed in a variety of applications. In particular, the nanotube devices of the present invention provide a new class of versatile chemical and biological sensors. The present invention describes methods for growing individual nanotubes in a controlled fashion and for manipulating and integrating the nanotubes into functional devices. It further provides methods for modifying the nanotubes such that their sensitivity to a wide range of chemical and biological species can be achieved.

WO 01/44796 A1

PATENT APPLICATION

CARBON NANOTUBE DEVICES

5

10 CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional/continuation-in-part of copending patent application 09/133,948 filed 8/14/98, which is herein incorporated by reference. This application is based on Provisional application 60/171,200 filed 12/15/99, which is 15 herein incorporated by reference.

STATEMENT REGARDING FEDERALLY SPONSORED
RESEARCH OR DEVELOPMENT

This invention was supported in part by grant number N00014-99-20 1-0495 from the Office of Naval Research. The Government has certain rights in the invention.

FIELD OF THE INVENTION

This invention relates generally to nanotube devices. More 25 particularly, it relates to a new class of nanotube chemical and biological sensors.

BACKGROUND ART

Sensing chemical and biological species plays an important role 30 in many industrial, agricultural, medical, and environmental processes. Detection of NO₂ gas, for example, provides a crucial measure of environmental pollution due to combustion or automotive emissions. The amount of NH₃ also needs to be closely monitored in industrial, medical and living

environments. Moreover, there is a growing need to detect biological species in a variety of biomedical applications.

Chemical sensors in the prior art commonly employ solid state 5 materials, such as semiconducting metal oxides, as sensing agents. The sensing is achieved by detecting change in electrical resistance of the sensor resulted from adsorption of foreign chemical species onto the sensing material. In order to achieve significant sensitivity, however, sensors of this 10 type must operate at elevated temperatures so to enhance chemical reactivity. Other drawbacks of these prior art sensors include long recovery times (if not rendering irreversibility), poor reproducibility, and very limited range of chemical species each sensor is able to detect.

15 In view of the above, there is a need in the art for sensing devices that provide not only significant and robust, but more advantageously, tunable response to a variety of chemical and biological species.

20 **OBJECTS AND ADVANTAGES OF THE INVENTION**
Accordingly, it is a principle object of the present invention to provide an assembly of novel and versatile nanotube devices that can be employed in a variety of applications. In 25 particular, these nanotube devices provide a new class of chemical and biological sensors. It is another object of this invention to provide methods for growing individually separable nanotubes in a controlled fashion. It is a further object of this invention to provide methods for manipulating and 30 integrating the nanotubes into functional devices. It is an additional object of this invention to provide methods for modifying the nanotubes so as to tune their sensitivity to a variety of molecular species.

A primary advantage of the present invention is that it provides a new class of electrical, mechanical, and electrochemical nanotube devices that can be individually tailored to a wide range of applications. Another unique

5 feature of the present invention is manifest in that these novel nanotube devices demonstrate significant and robust response, and more significantly, tunable selectivity to chemical or biological species in their environments.

10 These and other objects and advantages of the present invention will become more evident after consideration of the ensuing description and the accompanying drawings.

SUMMARY OF THE INVENTION

15 The present invention includes a device comprising a substrate and two catalyst islands disposed on the substrate. Each catalyst island is capable of growing nanotubes when exposed to a hydrocarbon gas at elevated temperatures. At least one nanotube forms between, with its two ends rooted in, the two

20 opposing islands. Metal electrodes are then placed to fully cover the catalyst islands and the two ends of the bridging nanotube, providing means for measuring electrical response of the nanotube.

25 The substrate is typically made of doped silicon with a layer of native oxide. The catalyst comprises Fe_2O_3 , and alumina nanoparticles. The catalytic island is typically about 3 - 5 microns in size. The nanotube is generally a single-walled carbon nanotube that can be semiconducting, or metallic. The

30 metal electrodes typically comprise an alloy of nickel-gold, or titanium-gold.

The nanotube thus produced can be further modified by coating, or decorating, it with one or more sensing agents, such as

metal particles, polymers, and biological species, which impart sensitivity to a particular molecular species.

5 The selectivity of the nanotube to chemical species can also be tuned physically, for example, by applying a gating voltage to a nanotube. The gating voltage effectively shifts the Fermi energy level of the nanotube, giving rise to change in electrical conductivity of the nanotube upon adsorption of foreign chemical species.

10 The present invention also includes a device comprising a substrate covered with a layer of catalyst material. The catalyst enables the growth of nanotubes when exposed to a hydrocarbon gas at elevated temperatures, yielding a film of 15 interconnected nanotubes disposed on the substrate. Two metal electrodes are then deposited onto the two opposing sides of the film, separated by a gap devoid of any metal. Such a nanotube film device can be easily produced in a scaled-up fashion with low cost.

20 The substrate in the above nanotube film device is typically made of quartz. The catalyst comprises Fe_2O_3 and alumina nanoparticles. The nanotubes are generally single-walled carbon nanotubes that are semiconducting, or metallic. The 25 metal electrodes typically comprise an alloy of nickel-gold, or titanium-gold.

The nanotube film may further be modified by coating, or 30 decorating, it with one or more sensing agents, so as to impart sensitivity to a particular species in its environment. The sensing agents include metal particles, polymers, and biological species.

The nanotube devices of the present invention demonstrate high sensitivity, robust response, and a tunable selectivity to a wide range of molecular species. They operate in gaseous and liquid environments.

5

The novel features of the present invention will be best understood from the following drawings and detailed description.

10

BRIEF DESCRIPTION OF THE FIGURES

FIGS. 1A-1C depict a method for synthesizing individually distinct nanotubes on a substrate according to an embodiment of the present invention;

FIG. 2 illustrates an exemplary embodiment of a nanotube device comprising a single nanotube according to the present invention.

FIGS. 3A-3B show a method for making a nanotube film device according another embodiment of the present invention;

FIG. 4 displays electrical response of a single nanotube device to NO_2 and NH_3 , respectively;

FIG. 5 shows electrical response of a gold-decorated single nanotube device to thiol vapor;

FIG. 6 displays electrical responses of an as-grown nanotube film device and a PMMA-coated nanotube film device to NO_2 gas;

FIGS. 7A-7B show electrical response of a gold-decorated nanotube film device to thiol vapor and the detection of avidin using a thiol-coated-gold-decorated nanotube film device; and

FIG. 8 displays the detection of H_2 using a platinum-modified nanotube film device.

DETAILED DESCRIPTION OF THE INVENTION

FIGS. 1A-1C illustrate a method for synthesizing individually distinct nanotubes on a silicon substrate that is patterned with catalyst islands according to a first embodiment of the present invention. The principle procedures of the method have been reported in the art by the inventors (Nature 395, 878 (1998)), incorporated herein by reference. First, a layer of resist 10 is disposed and patterned on a top surface of a substrate 11, as illustrated in FIG. 1A. The substrate 11 is made of doped silicon with a layer of native oxide. Patterning on the resist 10 is typically performed by electron-beam lithography, producing holes 12 that expose the underlying substrate 11. The holes 12 are typically 5 microns in size, spaced at a distance of 10 microns apart. Next, a few drops of a catalyst material are placed on the surface of the substrate 11, filling the holes 12. The catalyst preparation includes mixing 15 mg of alumina nanoparticles, 0.05 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 0.015 mmol of $\text{MoO}_2(\text{acac})_2$, in 15 ml of methanol. After the solvent (i.e., methanol) dries, the remaining resist is lifted off, revealing an array of isolated catalyst islands 13 on the substrate 11, as shown in FIG. 1B. The catalyst-patterned substrate is then heated in a tube furnace to above 900 °C while exposed to a flow of methane. Heating decomposes $\text{Fe}(\text{NO}_3)_3$ to Fe_2O_3 . The Fe_2O_3 /nanoparticles mixture is capable of catalyzing the growth of carbon nanotubes when exposed to methane gas at elevated temperatures. The carbon nanotubes thus grown are predominantly individually distinct, single-walled nanotubes with few structural defects. FIG. 1C shows these nanotubes 14 emanated from the catalyst islands 13 on the substrate 11. They are found to be substantially straight, typically extending up to more than 10 microns in length with diameters ranging from 1 - 3 nanometers. Moreover, a number of the nanotubes are bridging adjacent islands. A nanotube bridge forms when a tube growing from one catalyst island falls on and

interacts with another island during the synthesis process as described.

5 In general, the substrate can be made of a material selected from a group consisting of silicon, alumina, quartz, silica and silicon nitride. The catalyst islands comprise a material selected from a group including iron, molybdenum, cobalt, nickel, ruthenium, zinc and oxides thereof. The nanotubes can be semiconducting, or metallic.

10

In addition to carbon, nanotubes made of other materials (e.g., silicon) can also be grown by following a synthesis process similar to what is described above. Those skilled in the art will be able to implement the corresponding synthesis 15 procedures.

The nanotube chip thus produced can be incorporated into a variety of electronic and mechanical devices. A device comprising a single nanotube can also be readily made. Using 20 an AFM (atomic force microscopy) tip, the nanotubes bridging two catalyst islands are cut mechanically or electrically until a single tube remains. Electron-beam lithography is then employed to deposit metal electrodes onto the two catalyst islands bridged by the nanotube. The electrodes are typically 25 made of an alloy of nickel-gold, or titanium-gold. For example, they can be 20 nanometers of nickel with 60 nanometers gold on top. These electrodes provide electrical connections between the nanotube and macroscopic electronic circuits. FIG. 2 shows an exemplary embodiment of a nanotube device comprising a 30 single nanotube 20 disposed between two catalyst islands 21 on a substrate 22. Two metal electrodes 23 are made to fully cover respective catalyst islands 21, including the two ends 24 of the bridging nanotube 20.

FIGS. 3A-3B show a method for synthesizing a film of nanotubes on a substrate that is initially covered with a layer of catalyst according to a second embodiment of the present invention. First, a quartz substrate 30 is coated with a layer 5 of catalyst 31 by spin-coating, as shown in FIG. 3A. The catalyst is typically prepared by mixing 15 mg of alumina nanoparticles, 0.05 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 0.015 mmol of $\text{MoO}_2(\text{acac})_2$, in 15 ml of methanol. The catalyst-covered substrate is then heated to above 900 °C in a flow of methane, 10 yielding a film of interconnected single-walled carbon nanotubes 32 on the substrate, as shown in FIG. 3B. Two metal electrodes 33, each comprising 20 nanometers of titanium followed by 60 nanometer of gold, are then evaporated onto the nanotube film through a shadow mask, such that there is a 15 metal-free gap forming between the two electrodes 33. Such a nanotube film device can be easily produced in a scaled-up fashion with low cost.

The substrate in FIGS. 3A-3B is typically made of a material 20 selected from a group consisting of silicon, alumina, quartz, silica and silicon nitride. The catalyst islands comprise a material selected from a group including iron, molybdenum, cobalt, nickel, ruthenium, zinc and oxides thereof. The nanotubes can be semiconducting, or metallic. The electrodes is 25 typically made of an alloy of nickel-gold, or titanium-gold.

The nanotube devices described above can be further physically or chemically modified, so as to be tailored for a particular 30 application. A semiconducting or metallic carbon nanotube exhibits inherent change in electrical conductance when exposed to certain chemical gases, resulted from adsorption of the gas particles on the nanotube. More significantly, by depositing one or more sensing agents onto the nanotube, its sensitivity to a wide range of chemical and biological species can be

achieved. The selectivity of the nanotube to chemical species can be also tuned by applying a gating voltage to the nanotube. The gating voltage effectively shifts the Fermi energy level of the nanotube, enabling the nanotube to be more responsive to a particular species. The embodiments described hereinafter demonstrate the functionality and versatility of the novel nanotube devices of the present invention.

FIG. 4 displays electrical responses of a device comprising a semiconducting single-walled carbon nanotube to various amounts of NO_2 and NH_3 gas, respectively. The gas sensing is carried out by enclosing the device in a glass flask. The flask is equipped with electrical feedthrough that makes electrical connections between the device and the electrical measurement circuits on the outside. It also permits a flow of gas. A carrier gas (e.g., Ar or air), diluted with NO_2 or NH_3 , then flows through the flask, while the electrical response of the nanotube is recorded. The device displays fast and significant response to the arrival of NO_2 and NH_3 , respectively. Moreover, after each gas sensing measurement, the electrical characteristics of the nanotube is able to fully recover in a flow of pure carrier gas over a period of several hours.

FIG. 5 shows electrical response of a gold-decorated single nanotube to thiol vapor. Gold is deposited on the nanotube by evaporation. Since it does not wet carbon, the evaporated gold particles decorate, rather than forming a continuous layer on the nanotube. The observed response to thiol results from the presence of the gold particles in this case, since the carbon nanotube alone does not respond to thiol. Given that many biological molecules like to link themselves onto thiol, by attaching a layer of thiol to a gold-decorated nanotube, this composite system promises to be a versatile biological sensor.

FIG. 6 shows electrical responses of an as-grown nanotube film (mat) device and a PMMA (polymethylmethacrylate)-covered nanotube film (mat) device to NO₂ gas. The PMMA coating in the later case is typically about 100 nanometers thick, and its 5 presence significantly improves the sensitivity and the response time of the nanotube device to NO₂.

FIG. 7A displays electrical response of a gold-decorated nanotube film device to thiol vapor, and FIG. 7B shows the 10 detection of avidin (a protein) using a thiol-coated-gold-decorated film device. In this case, gold particles are first evaporated onto the nanotube film, followed by attaching a monolayer of thiol with carboxylic functional group to the gold particles. The presence of thiol modifies the electrical 15 conductance of the nanotube device. When exposed to avidin, the carboxylic groups of the thiol molecules like to be linked to avidin molecules via carbodimide chemistry, giving rise to further change in electrical conductance of the nanotube film device. Note that in this case, the nanotube device operates 20 in a liquid environment.

FIG. 8 shows the detection of H₂ using a platinum-modified nanotube film device. Platinum particles are deposited onto and 25 decorate the nanotubes film. It is their presence that enables the device to respond to H₂ molecules.

Moreover, by attaching an enzyme to a nanotube or a nanotube film, the corresponding enzyme-coated nanotube device displays 30 changes in its electrical conductance when exposed to glucose, and other biological species. This would have important implications in medicine. Sensing CO has also been achieved by using modified nanotube devices.

In additional to the sensing agents described above, other metal particles (e.g., nickel, rhodium, palladium, Ti₂), polymers, and biological species can be used as sensing agents to modify the sensitivity of nanotubes to chemical and 5 biological species.

Clearly, the capabilities of the nanotube devices of the present invention as chemical and biological sensors are not merely limited to the exemplary embodiments described above. 10 Furthermore, the nanotube devices of the present invention can be utilized as electrochemical, electromechanical and other functional devices.

It is also apparent to those skilled in the art that the above 15 embodiments of the present invention are illustrative in purpose and are in no way limiting the scope of the invention. Many alternations and improvements can be introduced to the above-described embodiments without going beyond the scope of the invention. Thus, the scope of the present invention should 20 be determined, not by examples given, but by the appended claims and their legal equivalents.

CLAIMS

What is claimed is:

1. 1. A nanotube device comprising at least one nanotube, wherein a first end of said nanotube is in electrical contact with a first conducting element and a second end of said nanotube is in electrical contact with a second conducting element.
2. 2. The nanotube device of claim 1 wherein said nanotube is a carbon nanotube
3. 3. The nanotube device of claim 2 wherein said nanotube is a single-walled nanotube.
4. 4. The nanotube device of claim 1 wherein said nanotube is a silicon nanotube
5. 5. The nanotube device of claim 1 wherein said nanotube is semiconducting.
6. 6. The nanotube device of claim 1 wherein said nanotube is metallic.
7. 7. The nanotube device of claim 1 wherein said nanotube is disposed on a surface.
8. 8. The nanotube device of claim 7 wherein said surface is a top surface of a substrate comprising a material selected from a group consisting of silicon, alumina, quartz, silica and silicon nitride.

1 9. The nanotube device of claim 8 wherein said
2 substrate comprises doped silicon covered with a
3 layer of native oxide.

1 10. The nanotube device of claim 1 wherein at least one of
2 said conducting elements comprises a catalyst island
3 covered by a metal electrode, and wherein at least one
4 of said ends of said nanotube is rooted in said
5 catalyst island and covered by said metal electrode.

1 11. The nanotube device of claim 10 wherein said catalyst
2 island comprises a material selected from a group
3 consisting of iron, molybdenum, cobalt, nickel,
4 ruthenium, zinc and oxides thereof.

1 12. The nanotube device of claim 10 wherein said catalyst
2 island comprises Fe_2O_3 and alumina nanoparticles.

1 13. The nanotube device of claim 10 wherein said catalyst
2 island is typically in the range of 3 - 5 microns in
3 size.

1 14. The nanotube device of claim 10 wherein said metal
2 electrode comprises an alloy of nickel-gold.

1 15. The nanotube device of claim 10 wherein said metal
2 electrode comprises an alloy of titanium-gold.

1 16. The nanotube device of claim 1 wherein at least one of
2 said conducting elements comprises a metal pad covering
3 at least one of said ends of said nanotube.

1 17. The nanotube device of claim 16 wherein said metal
2 pad comprises a material selected from the group

consisting of titanium, gold, aluminum, chromium, and platinum.

18. The nanotube device of claim 1 further comprises one or more sensing agents attached to said nanotube.

19. A nanotube apparatus comprising:

- a) a nanotube film, having a first side and a second side; and
- b) two metal electrodes placed on said first side and said second side of said nanotube film.

20. The nanotube apparatus of claim 19 wherein said nanotube film comprises interconnected carbon nanotubes.

21. The nanotube apparatus of claim 20 wherein said nanotube film comprises interconnected single-walled nanotubes.

22. The nanotube apparatus of claim 19 wherein said nanotube film comprises interconnected silicon nanotubes.

23. The nanotube apparatus of claim 19 wherein said nanotube film comprises semiconducting nanotubes.

24. The nanotube apparatus of claim 19 wherein said nanotube film comprises metallic nanotubes.

25. The nanotube apparatus of claim 19 wherein said nanotube film is disposed on a top surface of a substrate.

26. The nanotube apparatus of claim 25 wherein said substrate comprises a material selected from a group

consisting of silicon, alumina, quartz, silica and silicon nitride.

27. The nanotube apparatus of claim 26 wherein said substrate further comprises a catalyst layer on its top surface.

28. The nanotube apparatus of claim 27 wherein said catalyst layer comprises a material selected from a group consisting of iron, molybdenum, cobalt, nickel, ruthenium, zinc and oxides thereof.

29. The nanotube apparatus of claim 27 wherein said catalyst layer comprises Fe_2O_3 and alumina nanoparticles.

30. The nanotube apparatus of claim 19 wherein said metal electrodes comprise an alloy of nickel-gold.

31. The nanotube apparatus of claim 19 wherein said metal electrodes comprise an alloy of titanium-gold.

32. The nanotube apparatus of claim 19 wherein said metal electrodes are typically about 1 - 100 microns apart.

33. The nanotube apparatus of claim 19 further comprises one or more sensing agents attached to said nanotube film.

34. A molecular sensor comprising:

- a) a nanotube device comprising at least one carbon nanotube, wherein a first end of said nanotube is in electrical contact with a first conducting element

5 and a second end of said nanotube is in electrical
6 contact with a second conducting element; and

7 b) a coating of one or more sensing agents deposited on
8 said nanotube;

9 wherein said sensing agents are so chosen such that the
10 agents-coated nanotube responds to a particular molecular
11 species.

12

1 35. The molecular sensor of claim 34 wherein said one or
2 more sensing agents comprise one or more materials
3 selected from the group consisting of metal particles,
4 polymers, and biological species.

5

1 36. The molecular sensor of claim 35 wherein said group
2 includes gold, platinum, nickel, rhodium, palladium,
3 TiO_2 , thiol, and enzymes.

4

1 37. The molecular sensor of claim 34 wherein said nanotube
2 is semiconducting.

3

1 38. The molecular sensor of claim 37 further comprising a
2 voltage source applying a gating voltage to said
3 nanotube, wherein said gating voltage is so chosen
4 such that said nanotube biased with said gating
5 voltage responds to a particular molecular species.

6

1 39. The molecular sensor of claim 38 wherein said
2 gating voltage is typically in the range of -20 to
3 20 Volts.

4

1 40. A method of making a device comprising at least one carbon
2 nanotube, comprising the steps of:

3 a) disposing a layer of resist on a top surface of a
4 substrate;

- 5 b) patterning said resist with holes that expose the
- 6 underlying substrate;
- 7 c) filling said holes with a catalyst material;
- 8 d) removing a remainder of said resist, whereby an array
- 9 of catalyst islands are disposed on said substrate;
- 10 e) exposing said catalyst islands to a hydrocarbon gas
- 11 at an elevated temperature, such that individual
- 12 carbon nanotubes emanate from said catalyst islands
- 13 and a number of said nanotubes bridge adjacent
- 14 catalyst islands;
- 15 f) breaking all but one nanotube bridging two of said
- 16 adjacent catalyst islands; and
- 17 g) depositing metal electrodes onto said two of said
- 18 adjacent catalyst islands, such that said metal
- 19 electrodes fully cover said two of said adjacent
- 20 catalyst islands and further extend over first and
- 21 second ends of said one nanotube that are rooted in
- 22 said two of said adjacent catalyst islands.

- 23
- 1 41. The method of claim 40 wherein said substrate comprises
- 2 a material selected from a group consisting of silicon,
- 3 alumina, quartz, silica and silicon nitride.
- 4
- 1 42. The method of claim 40 wherein said catalyst islands
- 2 comprise a material selected from a group consisting of
- 3 iron, molybdenum, cobalt, nickel, ruthenium, zinc and
- 4 oxides thereof.
- 5
- 1 43. The method of claim 40 wherein said catalyst islands
- 2 comprises Fe_2O_3 and alumina nanoparticles.
- 3
- 1 44. The method of claim 40 wherein said catalyst islands
- 2 are typically in the range of 3-5 microns in size.
- 3

- 1 45. The method of claim 40 wherein said catalyst islands
- 2 are typically about 10 microns apart.
- 3
- 1 46. The method of claim 40 wherein said metal electrodes
- 2 comprise an alloy of nickel-gold.
- 3
- 1 47. The method of claim 40 wherein said metal electrodes
- 2 comprise an alloy of titanium-gold.
- 3
- 1 48. The method of claim 40 wherein said hydrocarbon gas
- 2 contains methane.
- 3
- 1 49. The method of claim 40 wherein said elevated
- 2 temperature is above 900 °C.
- 3
- 1 50. The method of claim 40 wherein said nanotube is a
- 2 single-walled carbon nanotube.
- 3
- 1 51. The method of claim 40 wherein said nanotube is
- 2 typically up to 3 nanometers in diameter.
- 3
- 1 52. The method of claim 40 wherein said nanotube is
- 2 typically up tens of microns in length.
- 3
- 1 53. The method of claim 40 wherein said nanotube is
- 2 semiconducting.
- 3
- 1 54. The method of claim 40 further comprising applying a
- 2 gating voltage to said nanotube, such that said
- 3 nanotube biased with said gating voltage responds to a
- 4 particular molecular species.
- 5
- 1 55. The method of claim 55 wherein said gating voltage is
- 2 typically in the range of -20 to 20 Volts.

3

1 56. The method of claim 40 wherein said nanotube is
2 metallic.

3

1 57. The method of claim 40 further comprising coating said
2 nanotube with one or more sensing agents, such that the
3 agents-coated nanotube responds to a particular
4 molecular species.

5

1 58. The method of claim 57 wherein said one or more
2 sensing agents comprise one or more materials
3 selected from the group consisting of metal
4 particles, polymers, and biological species.

5

1 59. The method of claim 58 wherein said group includes
2 gold, platinum, nickel, rhodium, palladium, TiO₂,
3 thiol, and enzymes.

4

1 60. A method for making an apparatus comprising a carbon
2 nanotube film, comprising the steps of:

- 3 a) coating a top surface of a substrate with a catalyst
4 layer;
- 5 b) exposing said catalyst-coated substrate to a
6 hydrocarbon gas at an elevated temperature, such that
7 a nanotube film comprising interconnected carbon
8 nanotubes is formed; and
- 9 c) depositing two metal electrodes on a first side and a
10 second side of said nanotube film.

11

1 61. The method of claim 60 wherein said substrate comprises
2 a material selected from a group consisting of silicon,
3 alumina, quartz, silica and silicon nitride.

4

- 1 45. The method of claim 40 wherein said catalyst islands
2 are typically about 10 microns apart.
- 3
- 1 46. The method of claim 40 wherein said metal electrodes
2 comprise an alloy of nickel-gold.
- 3
- 1 47. The method of claim 40 wherein said metal electrodes
2 comprise an alloy of titanium-gold.
- 3
- 1 48. The method of claim 40 wherein said hydrocarbon gas
2 contains methane.
- 3
- 1 49. The method of claim 40 wherein said elevated
2 temperature is above 900 °C.
- 3
- 1 50. The method of claim 40 wherein said nanotube is a
2 single-walled carbon nanotube.
- 3
- 1 51. The method of claim 40 wherein said nanotube is
2 typically up to 3 nanometers in diameter.
- 3
- 1 52. The method of claim 40 wherein said nanotube is
2 typically up tens of microns in length.
- 3
- 1 53. The method of claim 40 wherein said nanotube is
2 semiconducting.
- 3
- 1 54. The method of claim 40 further comprising applying a
2 gating voltage to said nanotube, such that said
3 nanotube biased with said gating voltage responds to a
4 particular molecular species.
- 5
- 1 55. The method of claim 55 wherein said gating voltage is
2 typically in the range of -20 to 20 Volts.

3

1 56. The method of claim 40 wherein said nanotube is
2 metallic.

3

1 57. The method of claim 40 further comprising coating said
2 nanotube with one or more sensing agents, such that the
3 agents-coated nanotube responds to a particular
4 molecular species.

5

1 58. The method of claim 57 wherein said one or more
2 sensing agents comprise one or more materials
3 selected from the group consisting of metal
4 particles, polymers, and biological species.

5

1 59. The method of claim 58 wherein said group includes
2 gold, platinum, nickel, rhodium, palladium, TiO_2 ,
3 thiol, and enzymes.

4

1 60. A method for making an apparatus comprising a carbon
2 nanotube film, comprising the steps of:

- 3 a) coating a top surface of a substrate with a catalyst
4 layer;
- 5 b) exposing said catalyst-coated substrate to a
6 hydrocarbon gas at an elevated temperature, such that
7 a nanotube film comprising interconnected carbon
8 nanotubes is formed; and
- 9 c) depositing two metal electrodes on a first side and a
10 second side of said nanotube film.

11

1 61. The method of claim 60 wherein said substrate comprises
2 a material selected from a group consisting of silicon,
3 alumina, quartz, silica and silicon nitride.

4

- 1 62. The method of claim 60 wherein said catalyst layer
- 2 comprises a material selected from a group consisting
- 3 of iron, molybdenum, cobalt, nickel, ruthenium, zinc
- 4 and oxides thereof.
- 5
- 1 63. The method of claim 60 wherein said catalyst layer
- 2 comprises Fe_2O_3 , and alumina nanoparticles.
- 3
- 1 64. The method of claim 60 wherein said metal electrodes
- 2 comprise an alloy of nickel-gold.
- 3
- 1 65. The method of claim 60 wherein said metal electrodes
- 2 comprise an alloy of titanium-gold.
- 3
- 1 66. The method of claim 60 wherein said metal electrodes
- 2 are typically about 1 - 100 microns apart.
- 3
- 1 67. The method of claim 60 wherein said hydrocarbon gas
- 2 contains methane.
- 3
- 1 68. The method of claim 60 wherein said elevated
- 2 temperature is above 900 °C.
- 3
- 1 69. The method of claim 60 wherein said nanotube film
- 2 comprises interconnected single-walled carbon
- 3 nanotubes.
- 4
- 1 70. The method of claim 60 wherein said nanotube film
- 2 comprises semiconducting nanotubes.
- 3
- 1 71. The method of claim 60 wherein said nanotube film
- 2 comprises metallic nanotubes.
- 3

1 72. The method of claim 60 further comprising coating said
2 nanotube film with one or more sensing agents, such
3 that the agents-coated nanotube film responds to a
4 particular molecular species.

1 73. The method of claim 72 wherein said one or more
2 sensing agents comprise one or more materials
3 selected from the group consisting of metal
4 particles, polymers, and biological species.

5
1 74. The method of claim 73 wherein said group includes
2 gold, platinum, nickel, rhodium, palladium, TiO₂,
3 thiol, and enzymes.

4
1 75. A sensing method comprising the steps of:

2 a) disposing a molecular sensor comprising at least one
3 carbon nanotube inside an enclosure, wherein a first
4 end of said nanotube is in electrical contact with a
5 first conducting element and a second end of said
6 nanotube is in electrical contact with a second
7 conducting element;
8 b) connecting said first and second conducting elements
9 to an electrical measurement circuit; and
10 c) introducing a molecular species to said enclosure,
11 while monitoring an electrical response of said
12 molecular sensor.

13
1 76. The sensing method of claim 75 wherein said molecular
2 species comprises a gas.

3
1 77. The sensing method of claim 75 wherein said molecular
2 species comprises a liquid.

1 78. The sensing method of 75 wherein said nanotube is
2 deposited with one or more sensing agents so to enable
3 said nanotube to respond to said molecular species.

4
1 79. The sensing method of 75 wherein said nanotube is
2 semiconducting, and wherein said nanotube is biased
3 with a gating voltage so to enable said nanotube to
4 respond to said molecular species.

5

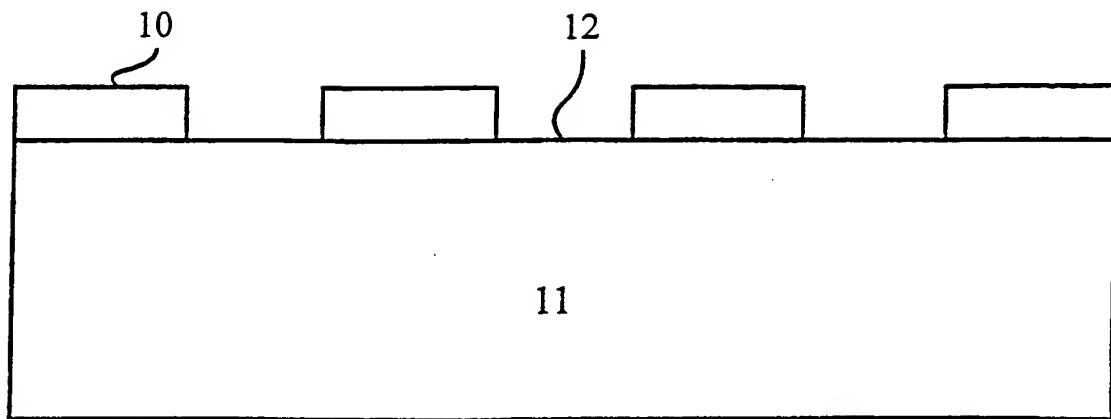


Fig. 1A

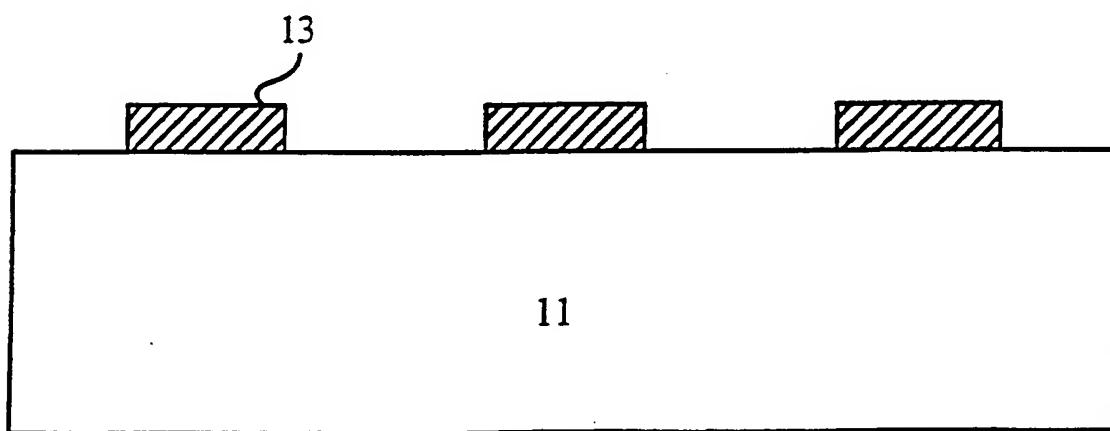


Fig. 1B

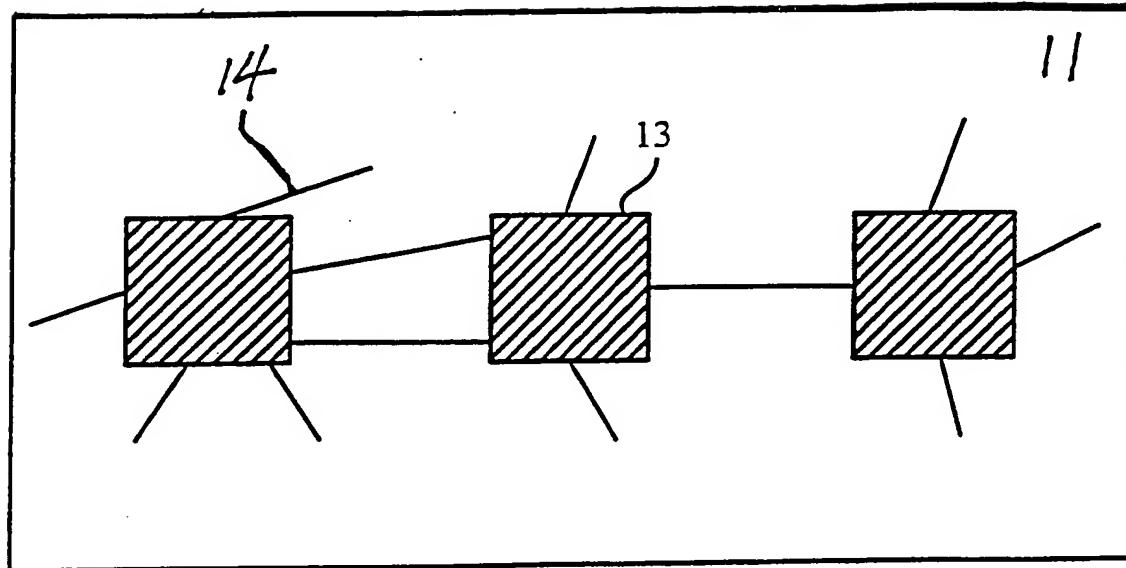


Fig. 1C

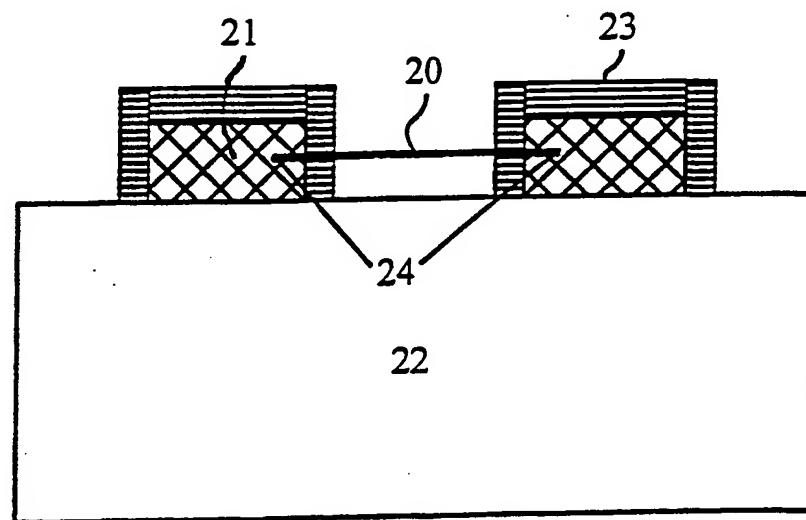


Fig. 2

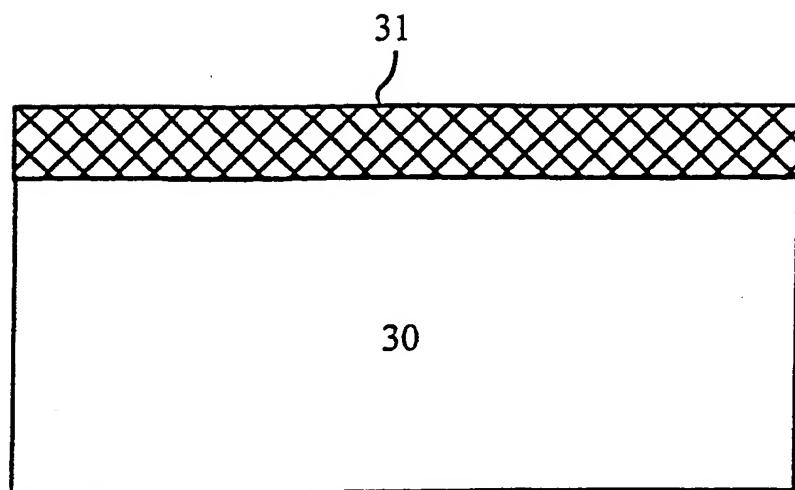


Fig. 3A

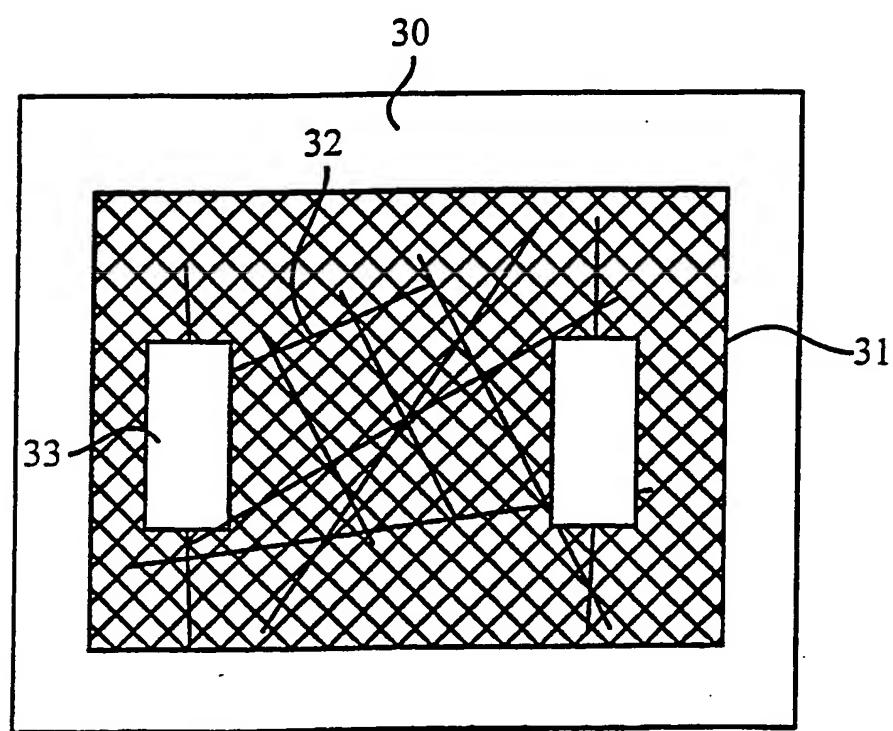
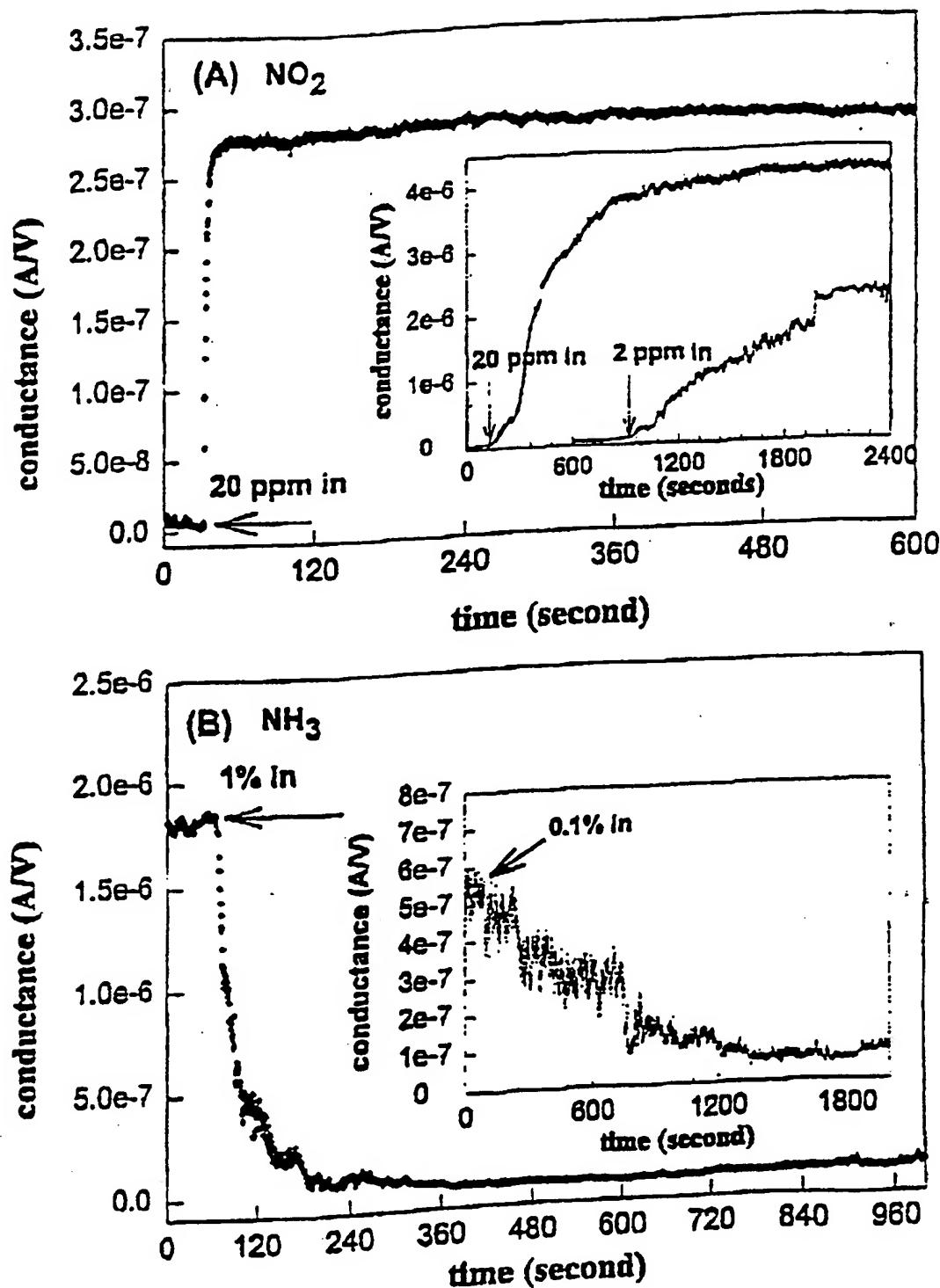


Fig. 3B



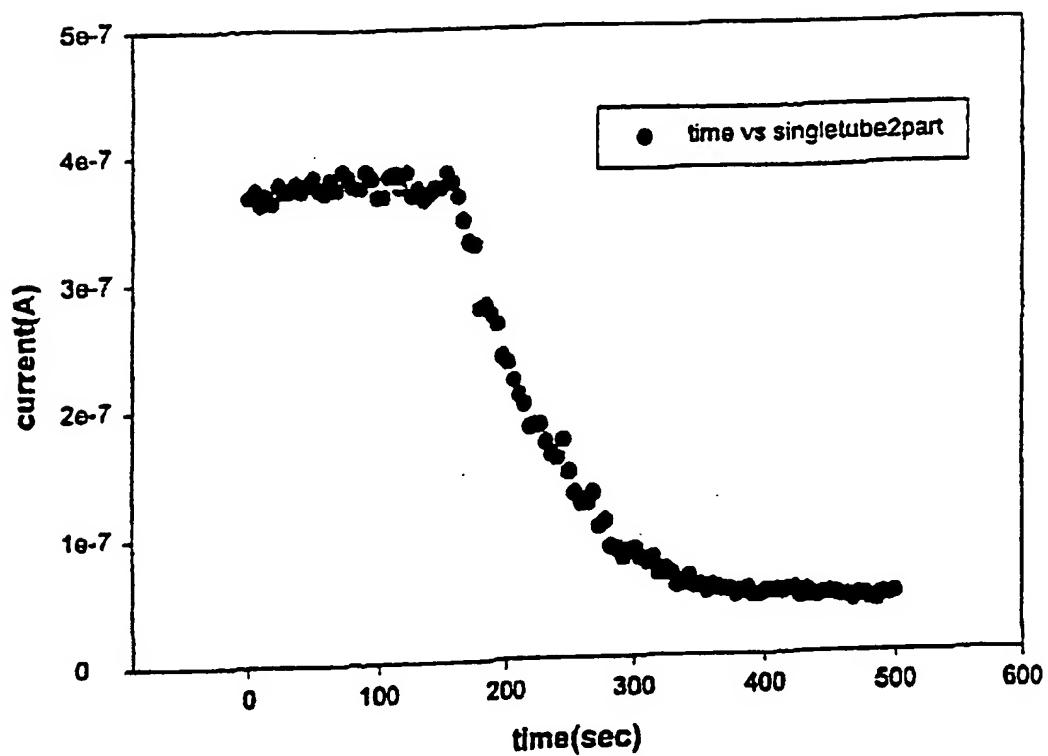
detection of thiol vapor using Au modified single tube

Fig. 5

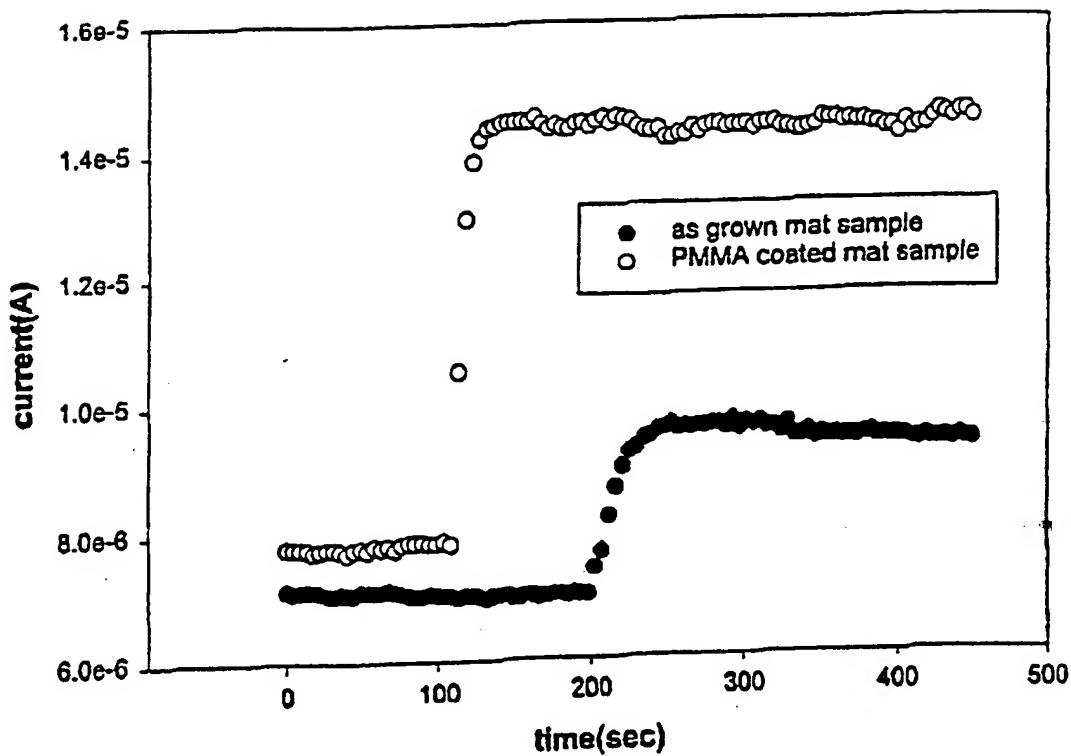
NO₂ sensing (2ppm)

Fig. 6

detection of thiol vapor using Au modified mat sample

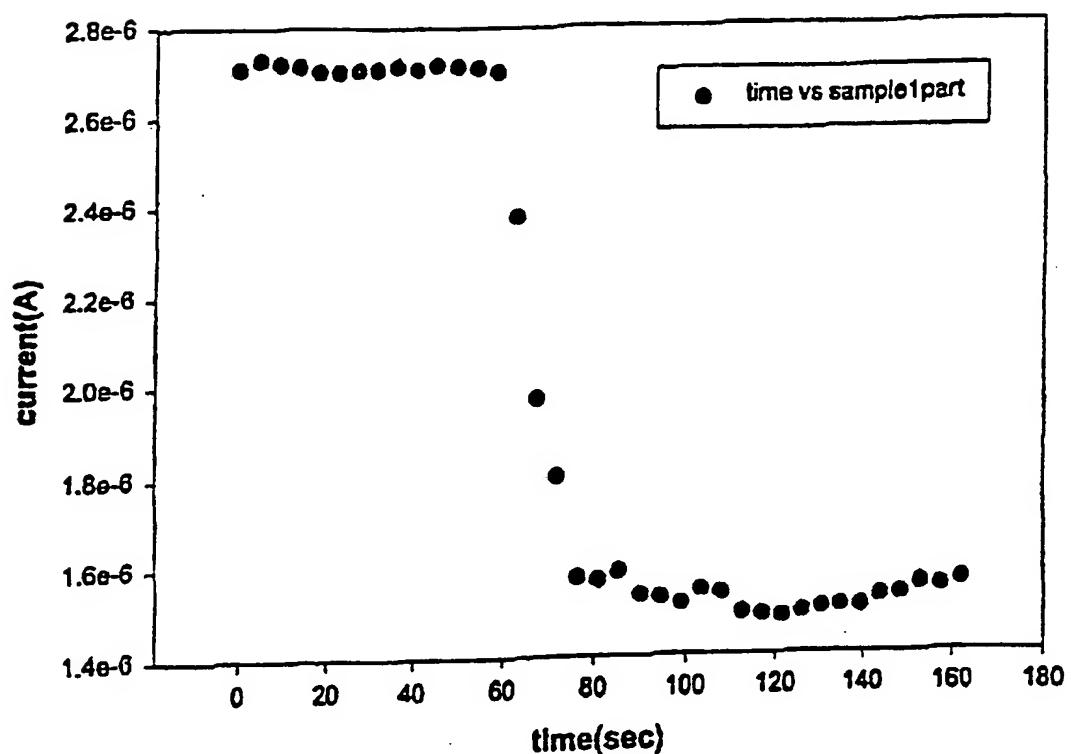


Fig. 7A

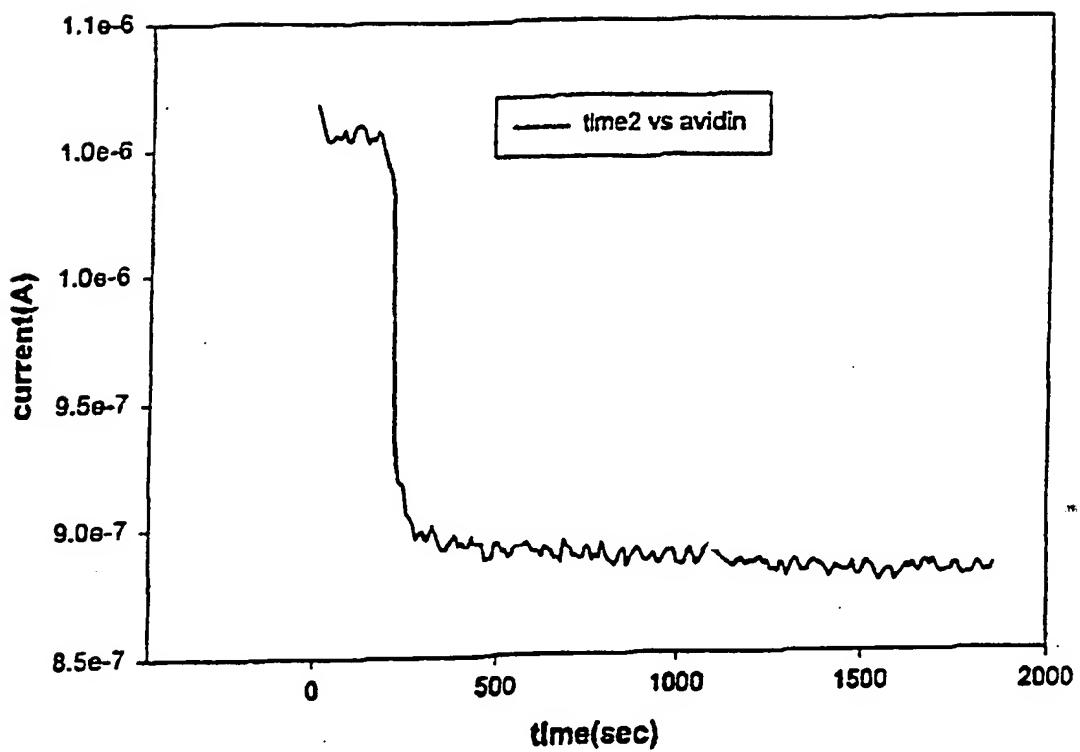
detection of avidin

Fig. 7B

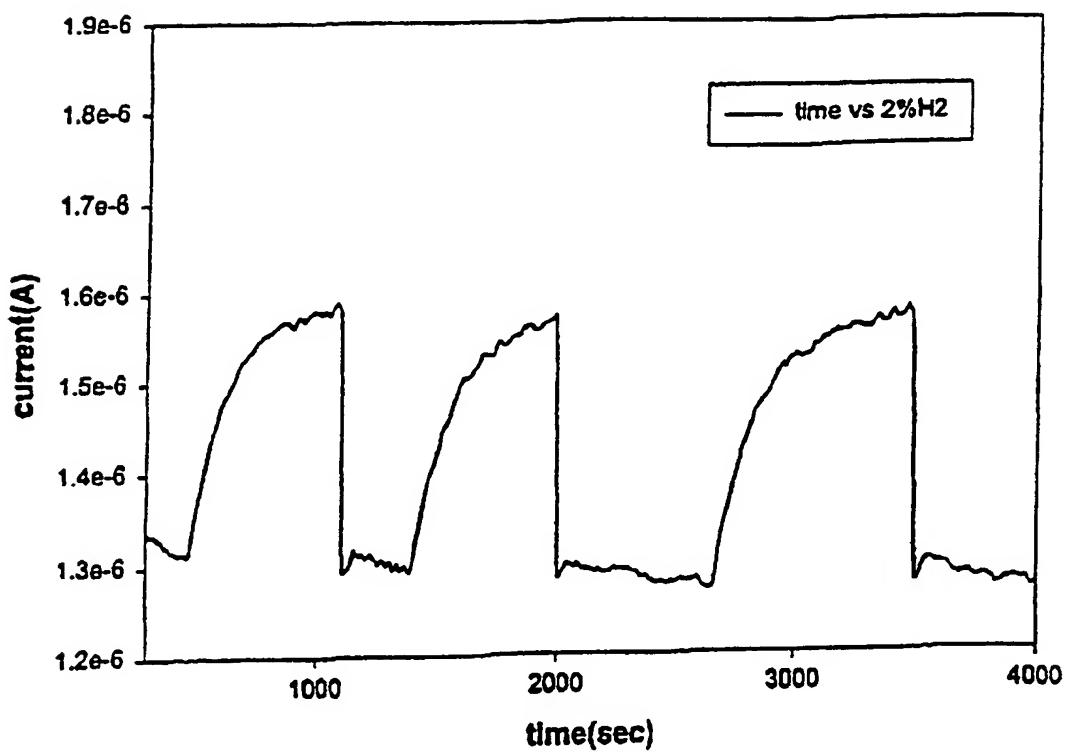
Detection of 2% H₂ in dry air

Fig. 8

INTERNATIONAL SEARCH REPORT

Final application No.
PCT/US00/42186

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G01N 27/12
US CL : 422/82.02, 90, 98; 436/151

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 422/82.02, 90, 98; 436/151

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST, CAS
search terms: nanotubes, electrodes, sensor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,334,351 A (HEINZE et al) 02 August 1994, entire document.	1-79
Y	US 5,866,434 A (MASSEY et al) 02 February 1999, entire document.	1-79
A	US 5,726,524 A (DEBE) 10 March 1998, entire document.	1-79
A	US 5,872,422 A (XU et al) 16 February 1999, entire document.	1-79
A	Dagani, "Much Ado About Nanotubes", C & E News, 11 January 1999, pages 31-34.	1-79
A	DAI et al., "Nanotubes as Nanoprobes in Scanning Probe Microscopy", Nature, Vol. 384, 14 November 1996, pages 147-150.	1-79

 Further documents are listed in the continuation of Box C. See patent family annex.

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

01 MAY 2001

Date of mailing of the international search report

17 MAY 2001

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JEFFREY R. SNAY

Telephone No. (703) 308-0661

THIS PAGE BLANK (USPTO)

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number
WO 01/44796 A1

(51) International Patent Classification⁷: G01N 27/12 (74) Agent: ALBOSZTA, Marek; 45 Cabot Ave., Suite 110, Santa Clara, CA 95051-6670 (US).

(21) International Application Number: PCT/US00/42186

(81) Designated State (national): JP.

(22) International Filing Date:
15 November 2000 (15.11.2000)

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(25) Filing Language: English

Published:
— with international search report

(30) Priority Data:
60/171,200 15 December 1999 (15.12.1999) US

(48) Date of publication of this corrected version:
4 October 2001

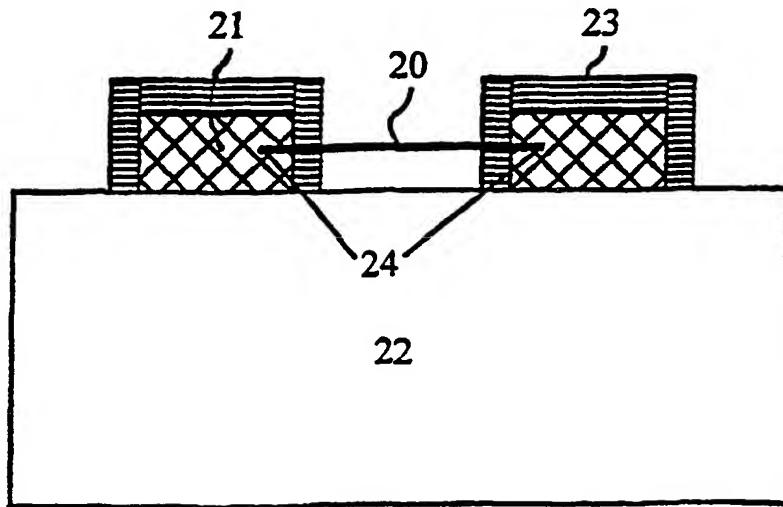
(71) Applicant: BOARD OF TRUSTEES OF THE LEAND STANFORD JUNIOR UNIVERSITY [US/US]; 900 Welch Road, Suite 350, Palo Alto, CA 94304 (US).

(15) Information about Correction:
see PCT Gazette No. 40/2001 of 4 October 2001, Section II

(72) Inventors: DAI, Hongjie; 365 Pescadero Tr., Sunnyvale, CA 94086 (US). KONG, Jing; 879 Roble Ave., Apt. 5, Menlo Park, CA 94062 (US).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CARBON NANOTUBE DEVICES



(57) Abstract: The invention provides an assembly of novel nanotube devices that can be employed in a variety of applications. In particular, the nanotube devices of the present invention provide a new class of versatile chemical and biological sensors. The device includes a nanotube (20) disposed between two catalyst islands (21) on a substrate (22). Two metal electrodes (23) are made to fully cover respective catalyst islands, including the two ends (24) of the bridging nanotube.

WO 01/44796 A1

THIS PAGE BLANK (USPTO)

CORRECTED VERSION(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number
WO 01/044796 A1(51) International Patent Classification⁷: **G01N 27/12** (74) Agent: ALBOSZTA, Marek; 45 Cabot Ave., Suite 110, Santa Clara, CA 95051-6670 (US).

(21) International Application Number: PCT/US00/42186

(81) Designated State (*national*): JP.(22) International Filing Date:
15 November 2000 (15.11.2000)(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(25) Filing Language: English

Published:

(26) Publication Language: English

— *with international search report*(30) Priority Data:
60/171,200 15 December 1999 (15.12.1999) US(48) Date of publication of this corrected version:
30 January 2003

(71) Applicant: BOARD OF TRUSTEES OF THE LEAND STANFORD JUNIOR UNIVERSITY [US/US]; 900 Welch Road, Suite 350, Palo Alto, CA 94304 (US).

(15) Information about Corrections:

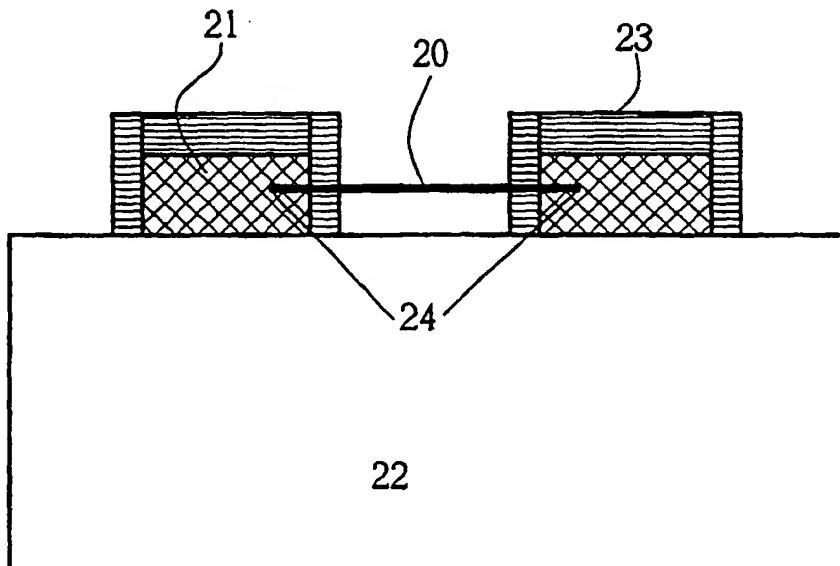
see PCT Gazette No. 05/2003 of 30 January 2003, Section II

(72) Inventors: DAI, Hongjie; 365 Pescadero Tr., Sunnyvale, CA 94086 (US). KONG, Jing; 879 Roble Ave., Apt. 5, Menlo Park, CA 94062 (US).

Previous Correction:
see PCT Gazette No. 40/2001 of 4 October 2001, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CARBON NANOTUBE DEVICES



(57) Abstract: The invention provides an assembly of novel nanotube devices that can be employed in a variety of applications. In particular, the nanotube devices of the present invention provide a new class of versatile chemical and biological sensors. The device includes a nanotube (20) disposed between two catalyst islands (21) on a substrate (22). Two metal electrodes (23) are made to fully cover respective catalyst islands, including the two ends (24) of the bridging nanotube.

WO 01/044796 A1

CARBON NANOTUBE DEVICES

5

10

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional/continuation-in-part of copending patent application 09/133,948 filed 8/14/98, which is herein incorporated by reference. This application is based on Provisional application 60/171,200 filed 12/15/99, which is 15 herein incorporated by reference.

**STATEMENT REGARDING FEDERALLY SPONSORED
RESEARCH OR DEVELOPMENT**

This invention was supported in part by grant number N00014-99-20 1-0495 from the Office of Naval Research. The Government has certain rights in the invention.

FIELD OF THE INVENTION

This invention relates generally to nanotube devices. More 25 particularly, it relates to a new class of nanotube chemical and biological sensors.

BACKGROUND ART

Sensing chemical and biological species plays an important role 30 in many industrial, agricultural, medical, and environmental processes. Detection of NO₂ gas, for example, provides a crucial measure of environmental pollution due to combustion or automotive emissions. The amount of NH₃ also needs to be closely monitored in industrial, medical and living

environments. Moreover, there is a growing need to detect biological species in a variety of biomedical applications.

Chemical sensors in the prior art commonly employ solid state 5 materials, such as semiconducting metal oxides, as sensing agents. The sensing is achieved by detecting change in electrical resistance of the sensor resulted from adsorption of foreign chemical species onto the sensing material. In order to achieve significant sensitivity, however, sensors of this 10 type must operate at elevated temperatures so to enhance chemical reactivity. Other drawbacks of these prior art sensors include long recovery times (if not rendering irreversibility), poor reproducibility, and very limited range of chemical species each sensor is able to detect.

15

In view of the above, there is a need in the art for sensing devices that provide not only significant and robust, but more advantageously, tunable response to a variety of chemical and biological species.

20

OBJECTS AND ADVANTAGES OF THE INVENTION

Accordingly, it is a principle object of the present invention to provide an assembly of novel and versatile nanotube devices that can be employed in a variety of applications. In 25 particular, these nanotube devices provide a new class of chemical and biological sensors. It is another object of this invention to provide methods for growing individually separable nanotubes in a controlled fashion. It is a further object of this invention to provide methods for manipulating and 30 integrating the nanotubes into functional devices. It is an additional object of this invention to provide methods for modifying the nanotubes so as to tune their sensitivity to a variety of molecular species.

A primary advantage of the present invention is that it provides a new class of electrical, mechanical, and electrochemical nanotube devices that can be individually tailored to a wide range of applications. Another unique 5 feature of the present invention is manifest in that these novel nanotube devices demonstrate significant and robust response, and more significantly, tunable selectivity to chemical or biological species in their environments.

10 These and other objects and advantages of the present invention will become more evident after consideration of the ensuing description and the accompanying drawings.

SUMMARY OF THE INVENTION

15 The present invention includes a device comprising a substrate and two catalyst islands disposed on the substrate. Each catalyst island is capable of growing nanotubes when exposed to a hydrocarbon gas at elevated temperatures. At least one nanotube forms between, with its two ends rooted in, the two 20 opposing islands. Metal electrodes are then placed to fully cover the catalyst islands and the two ends of the bridging nanotube, providing means for measuring electrical response of the nanotube.

25 The substrate is typically made of doped silicon with a layer of native oxide. The catalyst comprises Fe_2O_3 and alumina nanoparticles. The catalytic island is typically about 3 - 5 microns in size. The nanotube is generally a single-walled carbon nanotube that can be semiconducting, or metallic. The 30 metal electrodes typically comprise an alloy of nickel-gold, or titanium-gold.

The nanotube thus produced can be further modified by coating, or decorating, it with one or more sensing agents, such as

metal particles, polymers, and biological species, which impart sensitivity to a particular molecular species.

The selectivity of the nanotube to chemical species can also be tuned physically, for example, by applying a gating voltage to a nanotube. The gating voltage effectively shifts the Fermi energy level of the nanotube, giving rise to change in electrical conductivity of the nanotube upon adsorption of foreign chemical species.

10

The present invention also includes a device comprising a substrate covered with a layer of catalyst material. The catalyst enables the growth of nanotubes when exposed to a hydrocarbon gas at elevated temperatures, yielding a film of interconnected nanotubes disposed on the substrate. Two metal electrodes are then deposited onto the two opposing sides of the film, separated by a gap devoid of any metal. Such a nanotube film device can be easily produced in a scaled-up fashion with low cost.

20

The substrate in the above nanotube film device is typically made of quartz. The catalyst comprises Fe_2O_3 and alumina nanoparticles. The nanotubes are generally single-walled carbon nanotubes that are semiconducting, or metallic. The metal electrodes typically comprise an alloy of nickel-gold, or titanium-gold.

The nanotube film may further be modified by coating, or decorating, it with one or more sensing agents, so as to impart sensitivity to a particular species in its environment. The sensing agents include metal particles, polymers, and biological species.

The nanotube devices of the present invention demonstrate high sensitivity, robust response, and a tunable selectivity to a wide range of molecular species. They operate in gaseous and liquid environments.

5

The novel features of the present invention will be best understood from the following drawings and detailed description.

10

BRIEF DESCRIPTION OF THE FIGURES

FIGS. 1A-1C depict a method for synthesizing individually distinct nanotubes on a substrate according to an embodiment of the present invention;

FIG. 2 illustrates an exemplary embodiment of a nanotube device comprising a single nanotube according to the present invention.

FIGS. 3A-3B show a method for making a nanotube film device according another embodiment of the present invention;

FIG. 4 displays electrical response of a single nanotube device to NO₂ and NH₃, respectively;

FIG. 5 shows electrical response of a gold-decorated single nanotube device to thiol vapor;

FIG. 6 displays electrical responses of an as-grown nanotube film device and a PMMA-coated nanotube film device to NO₂ gas;

FIGS. 7A-7B show electrical response of a gold-decorated nanotube film device to thiol vapor and the detection of avidin using a thiol-coated-gold-decorated nanotube film device; and

FIG. 8 displays the detection of H₂ using a platinum-modified nanotube film device.

DETAILED DESCRIPTION OF THE INVENTION

FIGS. 1A-1C illustrate a method for synthesizing individually distinct nanotubes on a silicon substrate that is patterned with catalyst islands according to a first embodiment of the present invention. The principle procedures of the method have been reported in the art by the inventors (Nature 395, 878 (1998)), incorporated herein by reference. First, a layer of resist 10 is disposed and patterned on a top surface of a substrate 11, as illustrated in FIG. 1A. The substrate 11 is made of doped silicon with a layer of native oxide. Patterning on the resist 10 is typically performed by electron-beam lithography, producing holes 12 that expose the underlying substrate 11. The holes 12 are typically 5 microns in size, spaced at a distance of 10 microns apart. Next, a few drops of a catalyst material are placed on the surface of the substrate 11, filling the holes 12. The catalyst preparation includes mixing 15 mg of alumina nanoparticles, 0.05 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 0.015 mmol of $\text{MoO}_2(\text{acac})_2$, in 15 ml of methanol. After the solvent (i.e., methanol) dries, the remaining resist is lifted off, revealing an array of isolated catalyst islands 13 on the substrate 11, as shown in FIG. 1B. The catalyst-patterned substrate is then heated in a tube furnace to above 900 °C while exposed to a flow of methane. Heating decomposes $\text{Fe}(\text{NO}_3)_3$ to Fe_2O_3 . The Fe_2O_3 /nanoparticles mixture is capable of catalyzing the growth of carbon nanotubes when exposed to methane gas at elevated temperatures. The carbon nanotubes thus grown are predominantly individually distinct, single-walled nanotubes with few structural defects. FIG. 1C shows these nanotubes 14 emanated from the catalyst islands 13 on the substrate 11. They are found to be substantially straight, typically extending up to more than 10 microns in length with diameters ranging from 1 - 3 nanometers. Moreover, a number of the nanotubes are bridging adjacent islands. A nanotube bridge forms when a tube growing from one catalyst island falls on and

interacts with another island during the synthesis process as described.

5 In general, the substrate can be made of a material selected from a group consisting of silicon, alumina, quartz, silica and silicon nitride. The catalyst islands comprise a material selected from a group including iron, molybdenum, cobalt, nickel, ruthenium, zinc and oxides thereof. The nanotubes can be semiconducting, or metallic.

10

In addition to carbon, nanotubes made of other materials (e.g., silicon) can also be grown by following a synthesis process similar to what is described above. Those skilled in the art will be able to implement the corresponding synthesis 15 procedures.

20 The nanotube chip thus produced can be incorporated into a variety of electronic and mechanical devices. A device comprising a single nanotube can also be readily made. Using an AFM (atomic force microscopy) tip, the nanotubes bridging two catalyst islands are cut mechanically or electrically until a single tube remains. Electron-beam lithography is then employed to deposit metal electrodes onto the two catalyst 25 islands bridged by the nanotube. The electrodes are typically made of an alloy of nickel-gold, or titanium-gold. For example, they can be 20 nanometers of nickel with 60 nanometers gold on top. These electrodes provide electrical connections between the nanotube and macroscopic electronic circuits. FIG. 2 shows an exemplary embodiment of a nanotube device comprising a 30 single nanotube 20 disposed between two catalyst islands 21 on a substrate 22. Two metal electrodes 23 are made to fully cover respective catalyst islands 21, including the two ends 24 of the bridging nanotube 20.

FIGS. 3A-3B show a method for synthesizing a film of nanotubes on a substrate that is initially covered with a layer of catalyst according to a second embodiment of the present invention. First, a quartz substrate 30 is coated with a layer 5 of catalyst 31 by spin-coating, as shown in FIG. 3A. The catalyst is typically prepared by mixing 15 mg of alumina nanoparticles, 0.05 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 0.015 mmol of $\text{MoO}_2(\text{acac})_2$, in 15 ml of methanol. The catalyst-covered substrate is then heated to above 900 °C in a flow of methane, 10 yielding a film of interconnected single-walled carbon nanotubes 32 on the substrate, as shown in FIG. 3B. Two metal electrodes 33, each comprising 20 nanometers of titanium followed by 60 nanometer of gold, are then evaporated onto the nanotube film through a shadow mask, such that there is a 15 metal-free gap forming between the two electrodes 33. Such a nanotube film device can be easily produced in a scaled-up fashion with low cost.

The substrate in FIGS. 3A-3B is typically made of a material 20 selected from a group consisting of silicon, alumina, quartz, silica and silicon nitride. The catalyst islands comprise a material selected from a group including iron, molybdenum, cobalt, nickel, ruthenium, zinc and oxides thereof. The nanotubes can be semiconducting, or metallic. The electrodes is 25 typically made of an alloy of nickel-gold, or titanium-gold.

The nanotube devices described above can be further physically or chemically modified, so as to be tailored for a particular application. A semiconducting or metallic carbon nanotube 30 exhibits inherent change in electrical conductance when exposed to certain chemical gases, resulted from adsorption of the gas particles on the nanotube. More significantly, by depositing one or more sensing agents onto the nanotube, its sensitivity to a wide range of chemical and biological species can be

achieved. The selectivity of the nanotube to chemical species can be also tuned by applying a gating voltage to the nanotube. The gating voltage effectively shifts the Fermi energy level of the nanotube, enabling the nanotube to be more responsive to a 5 particular species. The embodiments described hereinafter demonstrate the functionality and versatility of the novel nanotube devices of the present invention.

FIG. 4 displays electrical responses of a device comprising a 10 semiconducting single-walled carbon nanotube to various amounts of NO_2 and NH_3 gas, respectively. The gas sensing is carried out by enclosing the device in a glass flask. The flask is equipped with electrical feedthrough that makes electrical connections between the device and the electrical measurement 15 circuits on the outside. It also permits a flow of gas. A carrier gas (e.g., Ar or air), diluted with NO_2 or NH_3 , then flows through the flask, while the electrical response of the nanotube is recorded. The device displays fast and significant response to the arrival of NO_2 and NH_3 , respectively. Moreover, 20 after each gas sensing measurement, the electrical characteristics of the nanotube is able to fully recover in a flow of pure carrier gas over a period of several hours.

FIG. 5 shows electrical response of a gold-decorated single 25 nanotube to thiol vapor. Gold is deposited on the nanotube by evaporation. Since it does not wet carbon, the evaporated gold particles decorate, rather than forming a continuous layer on the nanotube. The observed response to thiol results from the presence of the gold particles in this case, since the carbon 30 nanotube alone does not respond to thiol. Given that many biological molecules like to link themselves onto thiol, by attaching a layer of thiol to a gold-decorated nanotube, this composite system promises to be a versatile biological sensor.

FIG. 6 shows electrical responses of an as-grown nanotube film (mat) device and a PMMA (polymethylmethacrylate)-covered nanotube film (mat) device to NO₂ gas. The PMMA coating in the later case is typically about 100 nanometers thick, and its 5 presence significantly improves the sensitivity and the response time of the nanotube device to NO₂.

FIG. 7A displays electrical response of a gold-decorated nanotube film device to thiol vapor, and FIG. 7B shows the 10 detection of avidin (a protein) using a thiol-coated-gold-decorated film device. In this case, gold particles are first evaporated onto the nanotube film, followed by attaching a monolayer of thiol with carboxylic functional group to the gold particles. The presence of thiol modifies the electrical 15 conductance of the nanotube device. When exposed to avidin, the carboxylic groups of the thiol molecules like to be linked to avidin molecules via carbodiimide chemistry, giving rise to further change in electrical conductance of the nanotube film device. Note that in this case, the nanotube device operates 20 in a liquid environment.

FIG. 8 shows the detection of H₂ using a platinum-modified nanotube film device. Platinum particles are deposited onto and 25 decorate the nanotubes film. It is their presence that enables the device to respond to H₂ molecules.

Moreover, by attaching an enzyme to a nanotube or a nanotube film, the corresponding enzyme-coated nanotube device displays changes in its electrical conductance when exposed to glucose, 30 and other biological species. This would have important implications in medicine. Sensing CO has also been achieved by using modified nanotube devices.

In additional to the sensing agents described above, other metal particles (e.g., nickel, rhodium, palladium, Ti_2), polymers, and biological species can be used as sensing agents to modify the sensitivity of nanotubes to chemical and 5 biological species.

Clearly, the capabilities of the nanotube devices of the present invention as chemical and biological sensors are not merely limited to the exemplary embodiments described above. 10 Furthermore, the nanotube devices of the present invention can be utilized as electrochemical, electromechanical and other functional devices.

It is also apparent to those skilled in the art that the above 15 embodiments of the present invention are illustrative in purpose and are in no way limiting the scope of the invention. Many alternations and improvements can be introduced to the above-described embodiments without going beyond the scope of the invention. Thus, the scope of the present invention should 20 be determined, not by examples given, but by the appended claims and their legal equivalents.

CLAIMS

What is claimed is:

- 1 1. A nanotube device comprising at least one nanotube,
2 wherein a first end of said nanotube is in electrical
3 contact with a first conducting element and a second end
4 of said nanotube is in electrical contact with a second
5 conducting element.
- 6
- 1 2. The nanotube device of claim 1 wherein said nanotube is
2 a carbon nanotube
- 3
- 1 3. The nanotube device of claim 2 wherein said nanotube
2 is a single-walled nanotube.
- 3
- 1 4. The nanotube device of claim 1 wherein said nanotube is
2 a silicon nanotube
- 3
- 1 5. The nanotube device of claim 1 wherein said nanotube is
2 semiconducting.
- 3
- 1 6. The nanotube device of claim 1 wherein said nanotube is
2 metallic.
- 3
- 1 7. The nanotube device of claim 1 wherein said nanotube is
2 disposed on a surface.
- 3
- 1 8. The nanotube device of claim 7 wherein said surface
2 is a top surface of a substrate comprising a material
3 selected from a group consisting of silicon,
4 alumina, quartz, silica and silicon nitride.
- 5

- 1 9. The nanotube device of claim 8 wherein said
2 substrate comprises doped silicon covered with a
3 layer of native oxide.
- 4
- 1 10. The nanotube device of claim 1 wherein at least one of
2 said conducting elements comprises a catalyst island
3 covered by a metal electrode, and wherein at least one
4 of said ends of said nanotube is rooted in said
5 catalyst island and covered by said metal electrode.
- 6
- 1 11. The nanotube device of claim 10 wherein said catalyst
2 island comprises a material selected from a group
3 consisting of iron, molybdenum, cobalt, nickel,
4 ruthenium, zinc and oxides thereof.
- 5
- 1 12. The nanotube device of claim 10 wherein said catalyst
2 island comprises Fe_2O_3 and alumina nanoparticles.
- 3
- 1 13. The nanotube device of claim 10 wherein said catalyst
2 island is typically in the range of 3 - 5 microns in
3 size.
- 4
- 1 14. The nanotube device of claim 10 wherein said metal
2 electrode comprises an alloy of nickel-gold.
- 3
- 1 15. The nanotube device of claim 10 wherein said metal
2 electrode comprises an alloy of titanium-gold.
- 3
- 1 16. The nanotube device of claim 1 wherein at least one of
2 said conducting elements comprises a metal pad covering
3 at least one of said ends of said nanotube.
- 4
- 1 17. The nanotube device of claim 16 wherein said metal
2 pad comprises a material selected from the group

3 consisting of titanium, gold, aluminum, chromium, and
4 platinum.

5

1 18. The nanotube device of claim 1 further comprises one or
2 more sensing agents attached to said nanotube.

3

1 19. A nanotube apparatus comprising:

2 a) a nanotube film, having a first side and a second
3 side; and

4 b) two metal electrodes placed on said first side and
5 said second side of said nanotube film.

6

1 20. The nanotube apparatus of claim 19 wherein said nanotube
2 film comprises interconnected carbon nanotubes.

3

1 21. The nanotube apparatus of claim 20 wherein said
2 nanotube film comprises interconnected single-walled
3 nanotubes.

4

1 22. The nanotube apparatus of claim 19 wherein said nanotube
2 film comprises interconnected silicon nanotubes.

3

1 23. The nanotube apparatus of claim 19 wherein said nanotube
2 film comprises semiconducting nanotubes.

3

1 24. The nanotube apparatus of claim 19 wherein said nanotube
2 film comprises metallic nanotubes.

3

1 25. The nanotube apparatus of claim 19 wherein said nanotube
2 film is disposed on a top surface of a substrate.

3

1 26. The nanotube apparatus of claim 25 wherein said
2 substrate comprises a material selected from a group

3 consisting of silicon, alumina, quartz, silica and
4 silicon nitride.

5

1 27. The nanotube apparatus of claim 26 wherein said
2 substrate further comprises a catalyst layer on
3 its top surface.

4

1 28. The nanotube apparatus of claim 27 wherein said
2 catalyst layer comprises a material selected
3 from a group consisting of iron, molybdenum,
4 cobalt, nickel, ruthenium, zinc and oxides
5 thereof.

6

1 29. The nanotube apparatus of claim 27 wherein said
2 catalyst layer comprises Fe_2O_3 and alumina
3 nanoparticles.

4

1. 30. The nanotube apparatus of claim 19 wherein said metal
2 electrodes comprise an alloy of nickel-gold.

3

1 31. The nanotube apparatus of claim 19 wherein said metal
2 electrodes comprise an alloy of titanium-gold.

3

1 32. The nanotube apparatus of claim 19 wherein said metal
2 electrodes are typically about 1 - 100 microns apart.

3

1 53. The nanotube apparatus of claim 19 further comprises
2 one or more sensing agents attached to said nanotube
3 film.

4

1 34. A molecular sensor comprising:

2 a) a nanotube device comprising at least one carbon
3 nanotube, wherein a first end of said nanotube is in
4 electrical contact with a first conducting element

5 and a second end of said nanotube is in electrical
6 contact with a second conducting element; and

7 b) a coating of one or more sensing agents deposited on
8 said nanotube;

9 wherein said sensing agents are so chosen such that the
10 agents-coated nanotube responds to a particular molecular
11 species.

12

1 35. The molecular sensor of claim 34 wherein said one or
2 more sensing agents comprise one or more materials
3 selected from the group consisting of metal particles,
4 polymers, and biological species.

5

1 36. The molecular sensor of claim 35 wherein said group
2 includes gold, platinum, nickel, rhodium, palladium,
3 TiO_2 , thiol, and enzymes.

4

1 37. The molecular sensor of claim 34 wherein said nanotube
2 is semiconducting.

3

1 38. The molecular sensor of claim 37 further comprising a
2 voltage source applying a gating voltage to said
3 nanotube, wherein said gating voltage is so chosen
4 such that said nanotube biased with said gating
5 voltage responds to a particular molecular species.

6

1 39. The molecular sensor of claim 38 wherein said
2 gating voltage is typically in the range of -20 to
3 20 Volts.

4

1 40. A method of making a device comprising at least one carbon
2 nanotube, comprising the steps of:

3 a) disposing a layer of resist on a top surface of a
4 substrate;

5 b) patterning said resist with holes that expose the
6 underlying substrate;
7 c) filling said holes with a catalyst material;
8 d) removing a remainder of said resist, whereby an array
9 of catalyst islands are disposed on said substrate;
10 e) exposing said catalyst islands to a hydrocarbon gas
11 at an elevated temperature, such that individual
12 carbon nanotubes emanate from said catalyst islands
13 and a number of said nanotubes bridge adjacent
14 catalyst islands;
15 f) breaking all but one nanotube bridging two of said
16 adjacent catalyst islands; and
17 g) depositing metal electrodes onto said two of said
18 adjacent catalyst islands, such that said metal
19 electrodes fully cover said two of said adjacent
20 catalyst islands and further extend over first and
21 second ends of said one nanotube that are rooted in
22 said two of said adjacent catalyst islands.
23

1 41. The method of claim 40 wherein said substrate comprises
2 a material selected from a group consisting of silicon,
3 alumina, quartz, silica and silicon nitride.

1 42. The method of claim 40 wherein said catalyst islands
2 comprise a material selected from a group consisting of
3 iron, molybdenum, cobalt, nickel, ruthenium, zinc and
4 oxides thereof.

1 43. The method of claim 40 wherein said catalyst islands
2 comprises Fe_2O_3 and alumina nanoparticles.

1 44. The method of claim 40 wherein said catalyst islands
2 are typically in the range of 3-5 microns in size.
3

- 1 62. The method of claim 60 wherein said catalyst layer
- 2 comprises a material selected from a group consisting
- 3 of iron, molybdenum, cobalt, nickel, ruthenium, zinc
- 4 and oxides thereof.
- 5
- 1 63. The method of claim 60 wherein said catalyst layer
- 2 comprises Fe_2O_3 and alumina nanoparticles.
- 3
- 1 64. The method of claim 60 wherein said metal electrodes
- 2 comprise an alloy of nickel-gold.
- 3
- 1 65. The method of claim 60 wherein said metal electrodes
- 2 comprise an alloy of titanium-gold.
- 3
- 1 66. The method of claim 60 wherein said metal electrodes
- 2 are typically about 1 - 100 microns apart.
- 3
- 1 67. The method of claim 60 wherein said hydrocarbon gas
- 2 contains methane.
- 3
- 1 68. The method of claim 60 wherein said elevated
- 2 temperature is above 900 °C.
- 3
- 1 69. The method of claim 60 wherein said nanotube film
- 2 comprises interconnected single-walled carbon
- 3 nanotubes.
- 4
- 1 70. The method of claim 60 wherein said nanotube film
- 2 comprises semiconducting nanotubes.
- 3
- 1 71. The method of claim 60 wherein said nanotube film
- 2 comprises metallic nanotubes.
- 3

- 1 72. The method of claim 60 further comprising coating said
- 2 nanotube film with one or more sensing agents, such
- 3 that the agents-coated nanotube film responds to a
- 4 particular molecular species.
- 1 73. The method of claim 72 wherein said one or more
- 2 sensing agents comprise one or more materials
- 3 selected from the group consisting of metal
- 4 particles, polymers, and biological species.
- 5
- 1 74. The method of claim 73 wherein said group includes
- 2 gold, platinum, nickel, rhodium, palladium, TiO₂,
- 3 thiol, and enzymes.
- 4
- 1 75. A sensing method comprising the steps of:
 - 2 a) disposing a molecular sensor comprising at least one
 - 3 carbon nanotube inside an enclosure, wherein a first
 - 4 end of said nanotube is in electrical contact with a
 - 5 first conducting element and a second end of said
 - 6 nanotube is in electrical contact with a second
 - 7 conducting element;
 - 8 b) connecting said first and second conducting elements
 - 9 to an electrical measurement circuit; and
 - 10 c) introducing a molecular species to said enclosure,
 - 11 while monitoring an electrical response of said
 - 12 molecular sensor.
- 13
- 1 76. The sensing method of claim 75 wherein said molecular
- 2 species comprises a gas.
- 3
- 1 77. The sensing method of claim 75 wherein said molecular
- 2 species comprises a liquid.
- 3

1 78. The sensing method of 75 wherein said nanotube is
2 deposited with one or more sensing agents so to enable
3 said nanotube to respond to said molecular species.
4

1 79. The sensing method of 75 wherein said nanotube is
2 semiconducting, and wherein said nanotube is biased
3 with a gating voltage so to enable said nanotube to
4 respond to said molecular species.

1/9

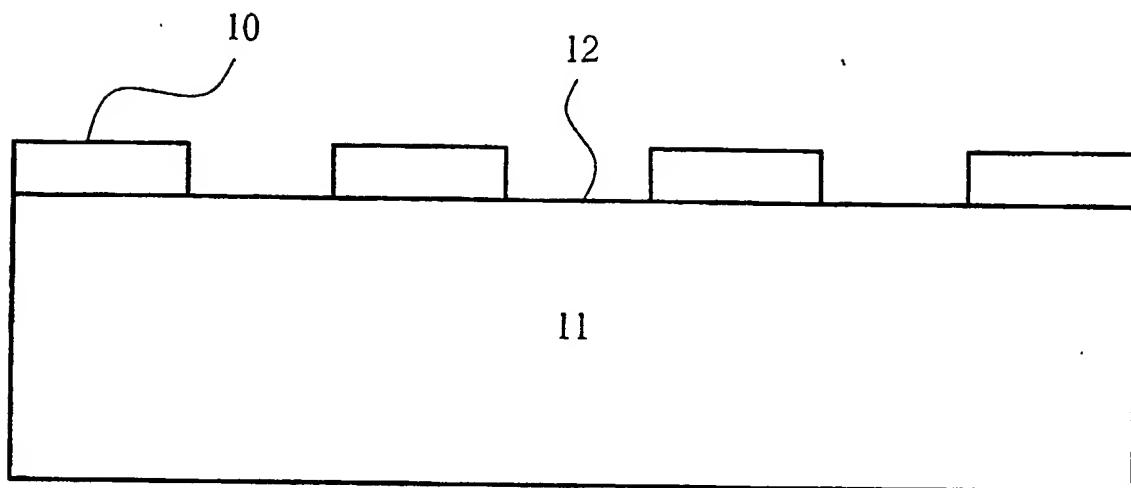


Fig. 1A

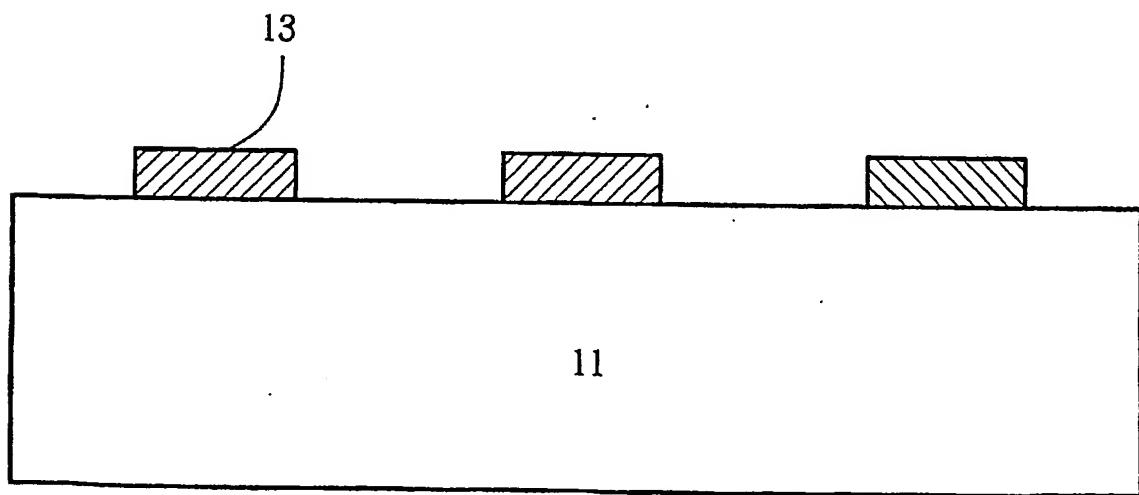


Fig. 1B

2/9

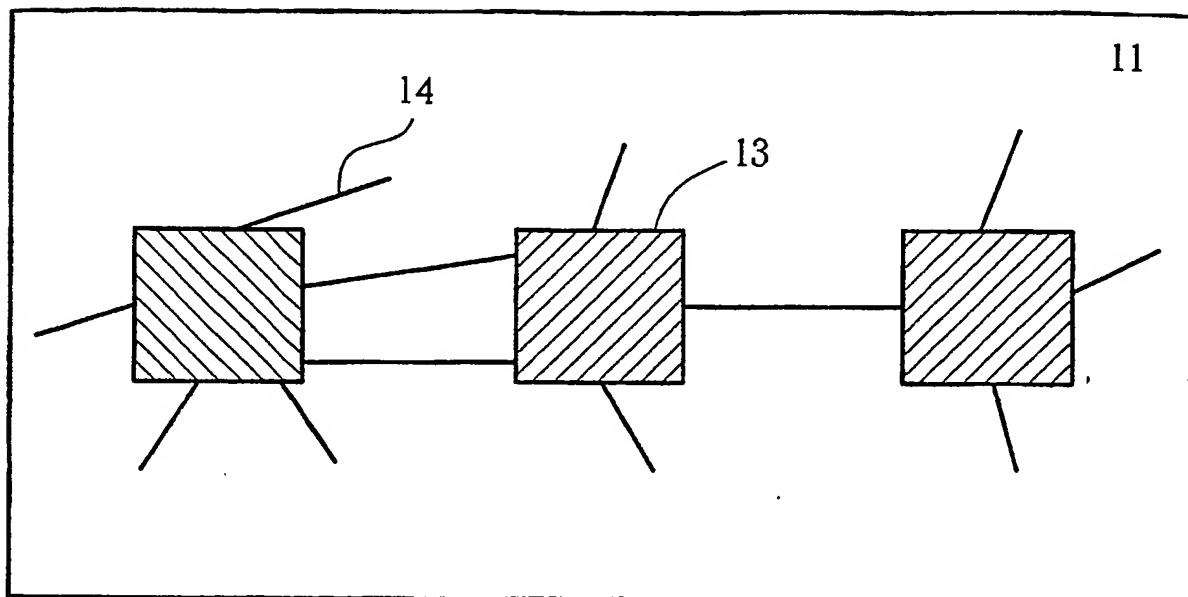


Fig. 1C

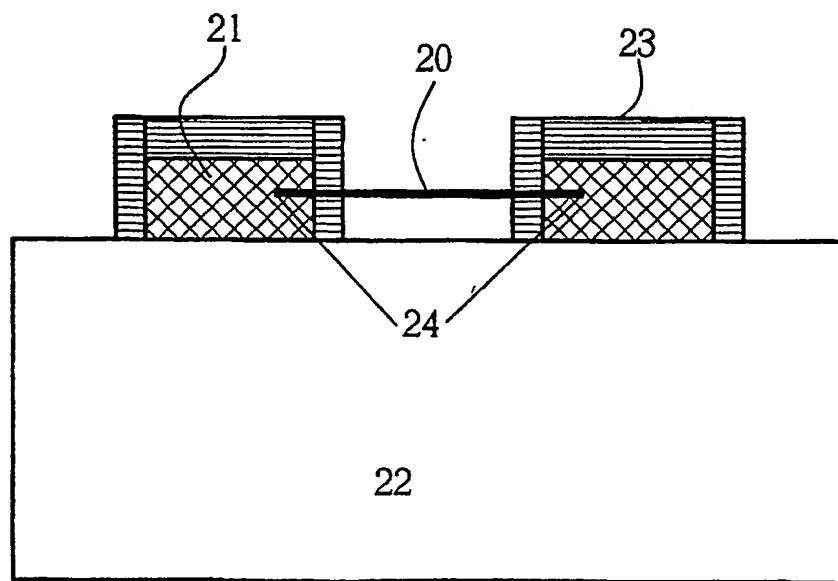


Fig. 2

3/9

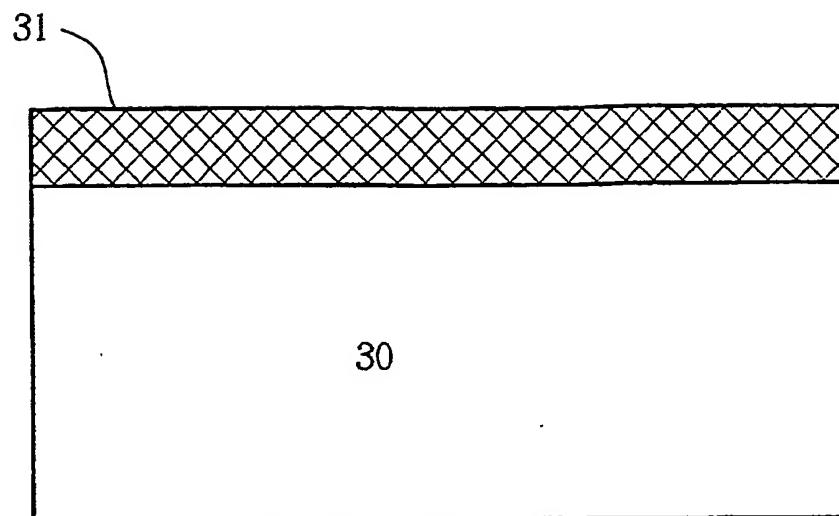


Fig. 3A

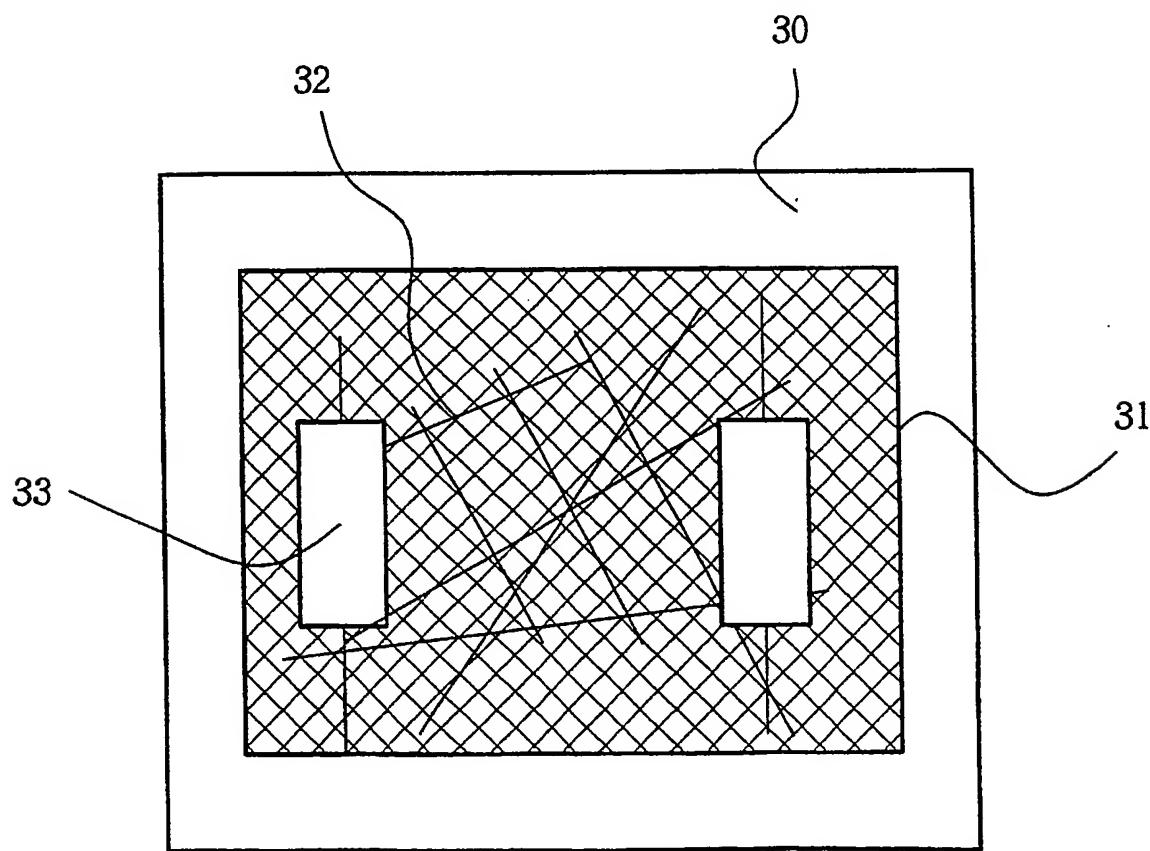


Fig. 3B

4/9

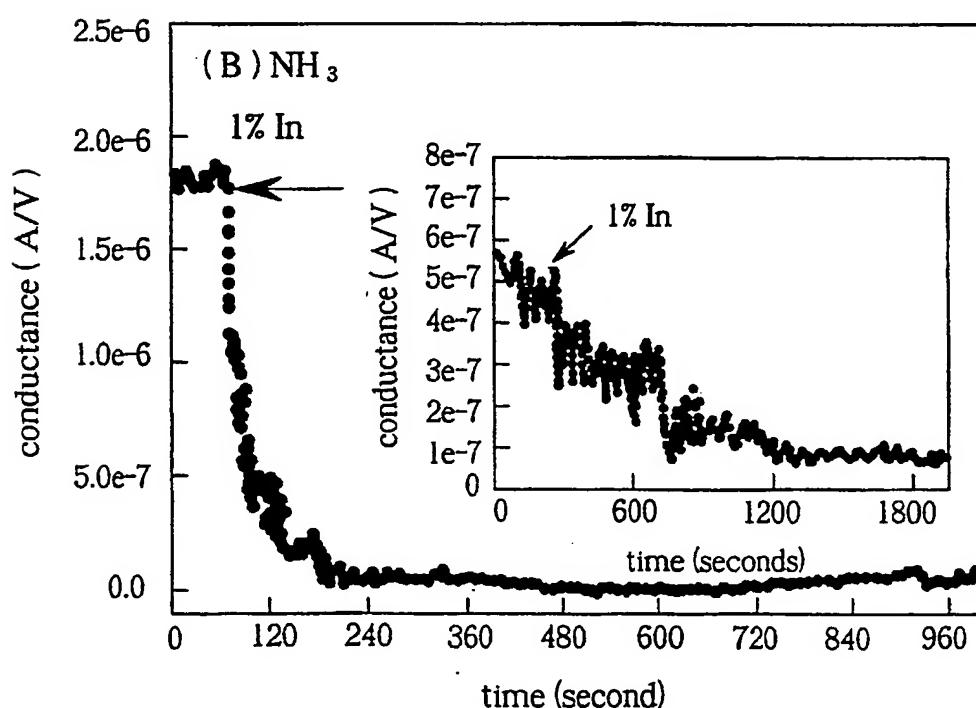
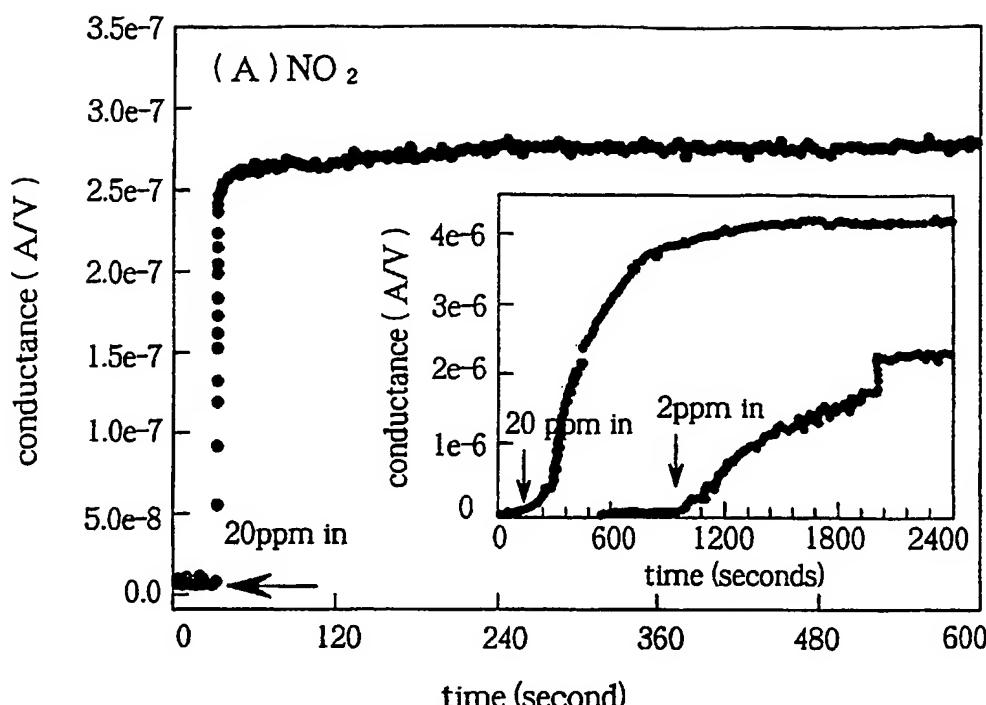


Fig. 4

5/9

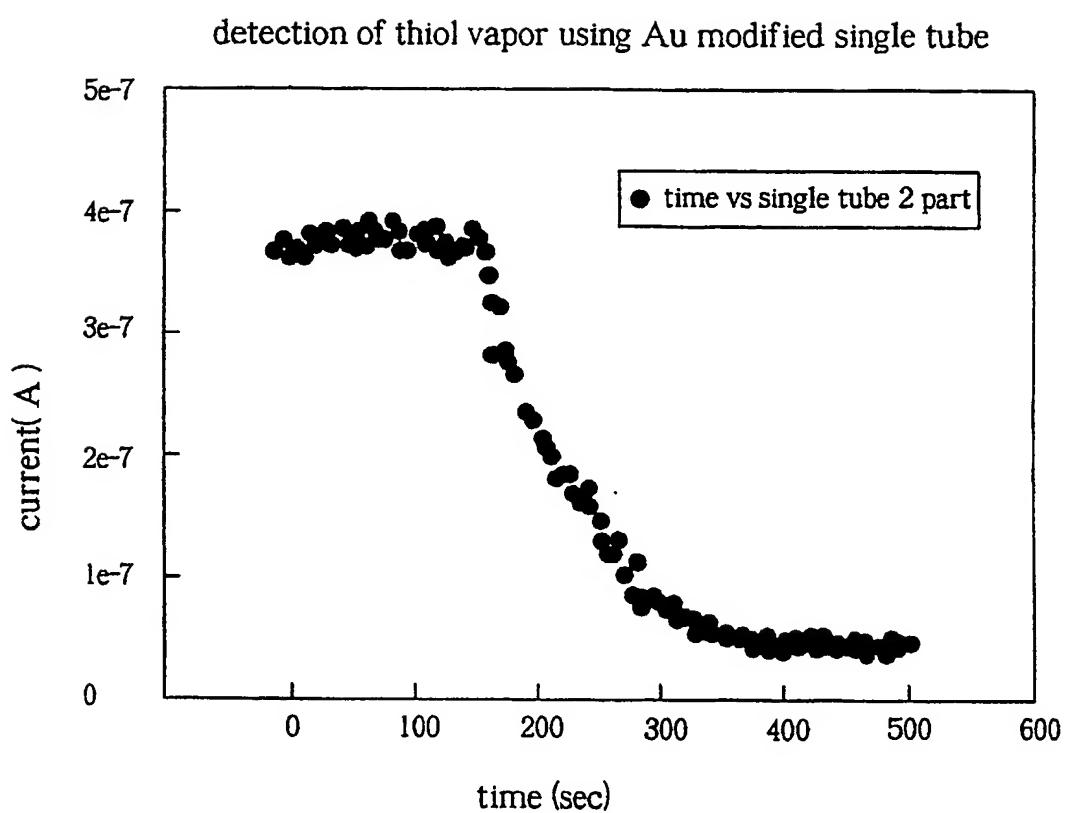


Fig. 5

6/9

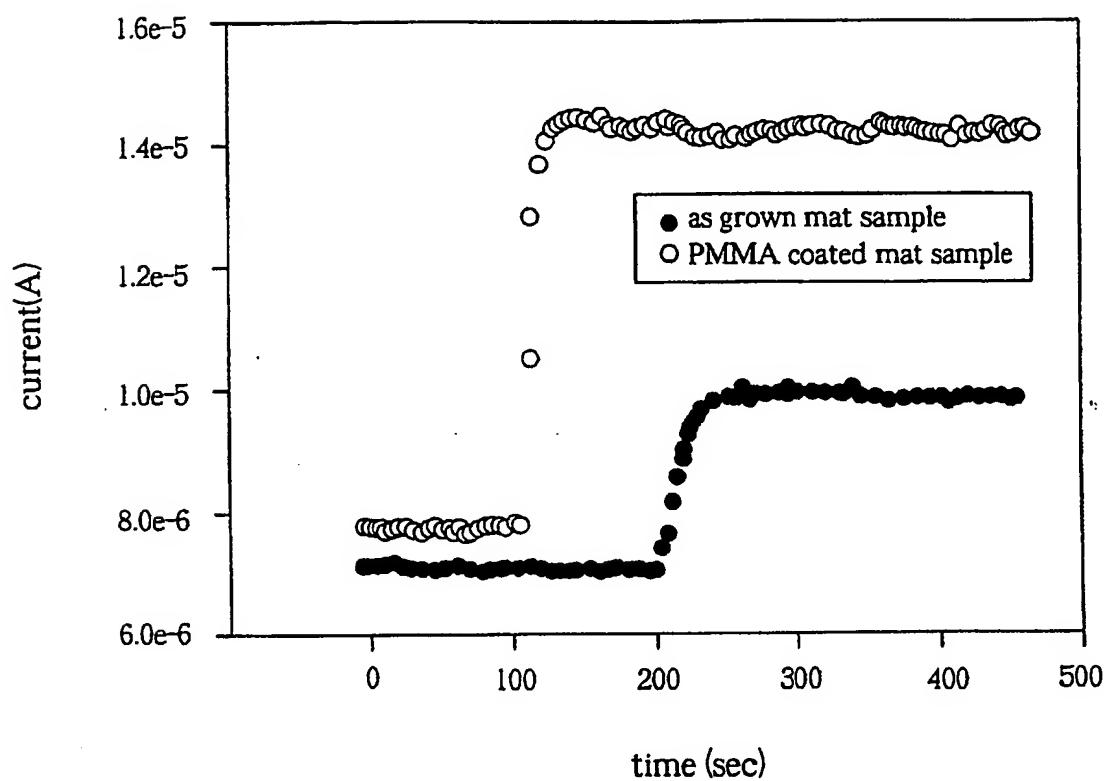
NO₂ sensimg (2ppm)

Fig. 6

7/9

detection of thiol vapor using Au modified mat sample

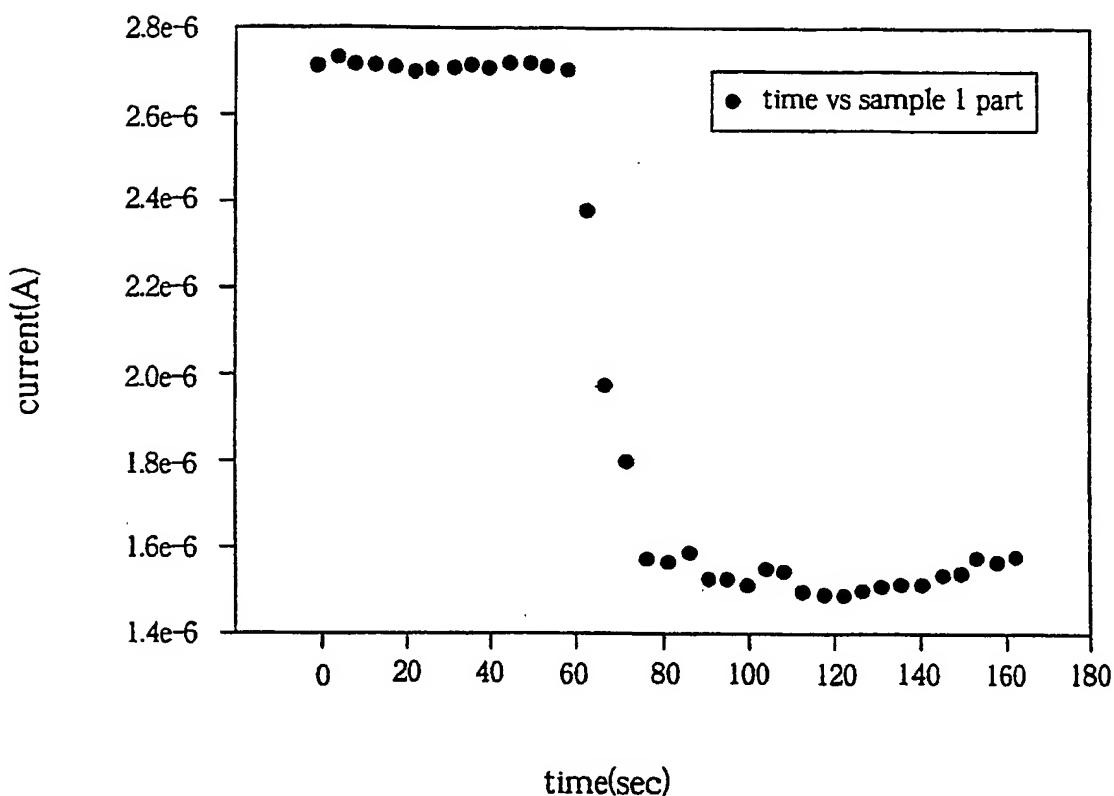


Fig. 7A

8/9

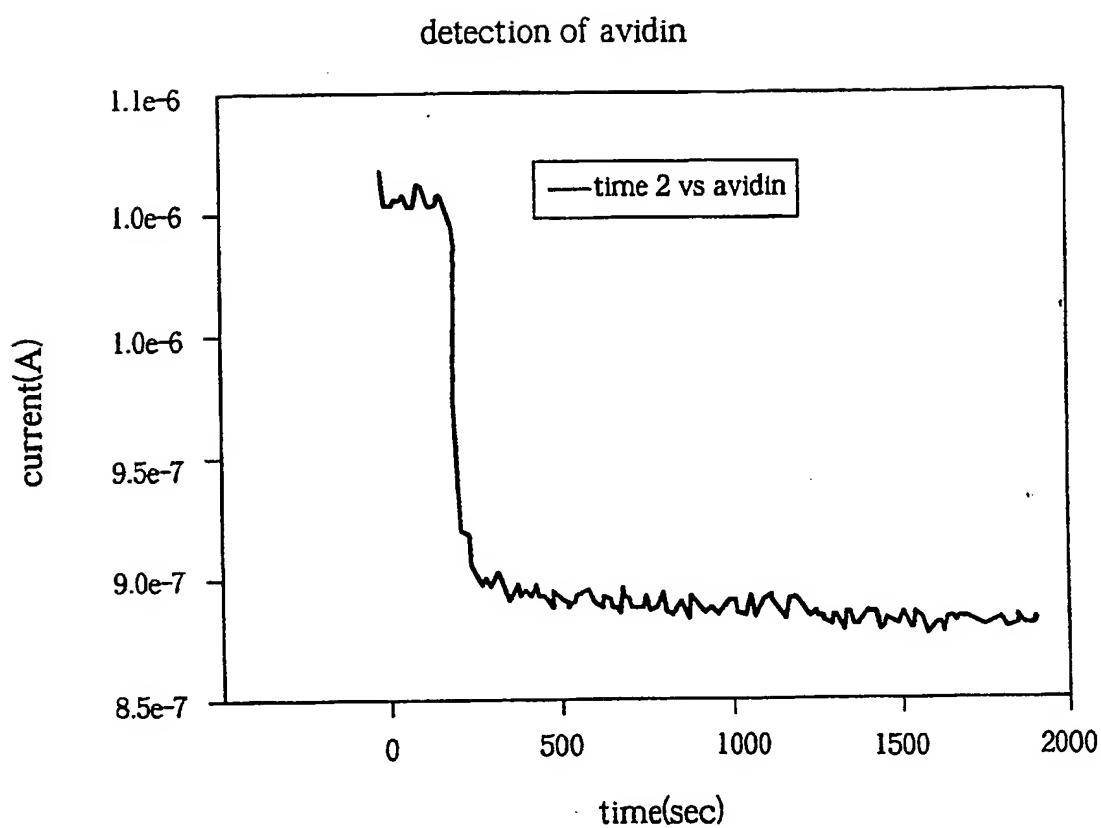


Fig. 7B.

9/9

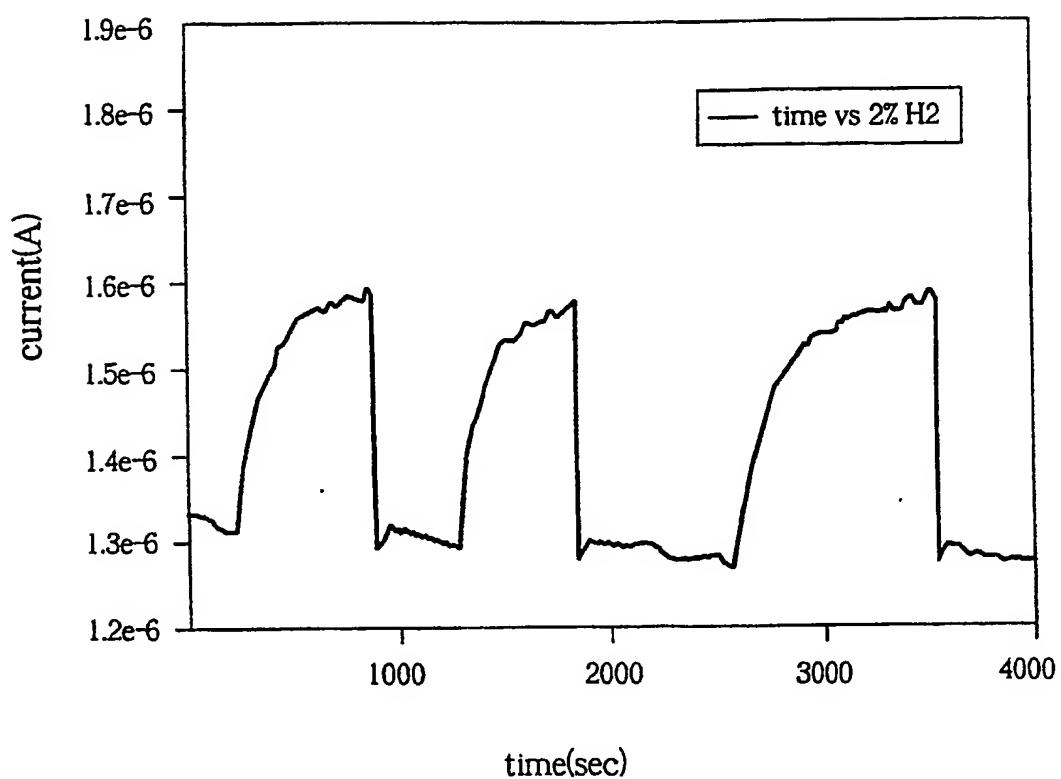
Detection of 2% H₂ in dry air

Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/42186

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G01N 27/12
US CL : 422/82.02, 90, 98; 436/151

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 422/82.02, 90, 98; 436/151

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST, CAS
search terms: nanotubes, electrodes, sensor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,334,351 A (HEINZE et al) 02 August 1994, entire document.	1-79
Y	US 5,866,434 A (MASSEY et al) 02 February 1999, entire document.	1-79
A	US 5,726,524 A (DEBE) 10 March 1998, entire document.	1-79
A	US 5,872,422 A (XU et al) 16 February 1999, entire document.	1-79
A	Dagani, "Much Ado About Nanotubes", C & E News, 11 January 1999, pages 31-34.	1-79
A	DAI et al., "Nanotubes as Nanoprobes in Scanning Probe Microscopy", Nature, Vol. 384, 14 November 1996, pages 147-150.	1-79

 Further documents are listed in the continuation of Box C. See patent family annex.

Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

01 MAY 2001

Date of mailing of the international search report

17 MAY 2001

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JEFFREY R. SNAY

Telephone No. (703) 308-0661

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)